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A radioactive mineral from Mozambique related to davidite.

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EARLY in 1947 a black, opaque, radioactive mineral resembling samarskite in appearance was discovered at Mavuzi in the Tete district of Mozambique, Portuguese East Africa. Two small specimens, one a rough twinned crystal with trigonal symmetry (fig. 3), were sent by A. M. Macgregor, then Director of the Geological Survey of Southern Rhodesia, to the British Museum (Natural History) for investigation, and a chemical analysis by E. Golding (table I, no. 2) followed later in the same year. X-ray photographs of fragments and powder from both specimens were taken, but revealed on development no diffraction spots, lines, or haloes. Only after prolonged heat-treatment could powder lines characteristic of crystalline material be obtained. The metamict nature of the mineral before heat-treatment is not unexpected in view of its chemical composition, optical isotropy, and glassy fracture.

Subsequently, a quantity of larger crystals and also massive material was received by the Geological Survey of Great Britain, making possible a more detailed study of the morphology, the chemical composition, and of the X-ray patterns of the mineral after heat-treatment. It was recognized by Dr. C. F. Davidson that chemically the radioactive mineral from Tete is very similar to davidite from Radium Hill, 20 miles ESE. of Olary, South Australia. The latter occurs as rough cuboidal crystals embedded in late quartz in a hydrothermal lode composed mainly of

[1] Communicated by permission of the Director.

biotite and a titanium-rich iron-ore complex, in part uraniferous.[1] The X-ray powder photographs of the two minerals after heat-treatment in a neutral atmosphere, however, show distinct differences. It is the purpose of this paper to describe the Tete mineral and to compare it with davidite.

The geology of the Tete area was investigated in 1948 by Dr. C. F. Davidson and Dr. J. A. E. Bennett, of the Geological Survey of Great Britain, who state that the dominant rocks are pre-Karroo norites and anorthosites, which were sheared to epidiorite and possibly to saussurite-rock along a number of shear zones. These formed the channels for later mineralizing fluids which altered the sheared rock, producing epidiorite with scapolite and a massive scapolite-calcite or scapolite-dolomite facies. The scapolite-carbonate associations carry the bulk of the radioactive ore, together with rutile, sphene, magnetite, ilmenite, apatite, and molybdenite.

Morphological crystallography (J. E. T. H.).—The mineral usually occurs massive, but sufficient specimens showing crystal faces have been found for some conclusions to be drawn regarding the morphological crystallography. Owing to the roughness of the faces, it has only been possible to make measurements with a contact goniometer, but the mineral appears to belong to the ditrigonal pyramidal class ($3m$) of the trigonal system. The forms have been indexed by adopting an axial ratio $a:c$ of 1:1·37, which corresponds to a polar ratio $p_0:r_0$ of 1·58:1. A table of forms and angles is given below. The conventions followed are those of Dana's

Forms.	Lower.	Upper.	ϕ.	ρ.
Pedions:	$\bar{c}$	c (0001)	—	0°
Ditrigonal prisms:		h (21$\bar{3}$0)	11°	90
		$-h$ (12$\bar{3}$0)	−11	90
		$-l$ (25$\bar{7}$0)	−14	90
Trigonal pyramid:	$-\bar{n}$	(03$\bar{3}$4)	−30	50
Hexagonal pyramids:		o (11$\bar{2}$1)	0	70
	$\bar{p}$	(22$\bar{4}$1)	0	80
Ditrigonal pyramids:		s (52$\bar{7}$8)	14	51
		t (41$\bar{5}$6)	19	50
		$-u$ (34$\bar{7}$3)	−5	73
	$-\bar{v}$	(34$\bar{7}$2)	−5	78
	$-\bar{w}$	(12$\bar{3}$3)	−11	54
	$-\bar{x}$	(26$\bar{8}$9)	−16	52
	$-\bar{y}$	(13$\bar{4}$4)	−16	55
	$-\bar{z}$	(16$\bar{7}$8)	−22	52

[1] D. Mawson, Mineral Notes. Trans. Roy. Soc. South Australia, 1916, vol. 40, pp. 262–266; The nature and occurrence of uraniferous mineral deposits in South Australia. Ibid., 1944, vol. 68, pp. 334–357. [M.A. **1**–69, **9**–250.]

'System of mineralogy', 7th edition (1944, vol. 1, p. 7). A bar over a letter means a form on the lower portion of the crystal; a bar under a letter (figs. 1–4) indicates a face in twinned position.

In habit the crystals are tabular to pyramidal, with ditrigonal pyramids dominant. They are sometimes found in irregular clusters (fig. 2). Twinning occurs by rotation about the axis [11$\bar{2}$0], as in pyrargyrite. The hemimorphic character is evident in single individuals and in interpenetrant twins, but well-developed aggregate twins are of apparent holohedral symmetry (figs. 1 A, B, and C). Some of the crystals are very large. For instance, the fragment illustrated in fig. 4 and idealized in fig. 1 B, is 12 inches long and weighs 22 pounds; it is estimated that the original crystal, if fully developed, was 19 inches across and weighed 100 pounds.

The small cuboidal crystals in which davidite occurs at Olary are too rough to be measured, but it is clear that they are quite unlike the Tete mineral in habit. Nevertheless, a cuboidal habit is not necessarily inconsistent with $3m$ symmetry, for assuming an axial ratio of 1:1·37 an aggregate twin of the form (10$\bar{1}$1) about [11$\bar{2}$0] is a rhombohedron of rhomb angle 85° 40′.

Physical properties.—The determination of the physical properties of the Tete mineral confirms the preliminary measurements of N. E. Barlow, of the Geological Survey of Southern Rhodesia. It has a subconchoidal fracture with no cleavage, a hardness of 6 (Mohs's scale), and a specific gravity of 4·46. The mineral is opaque, except at the extreme edges of very thin splinters, where it is translucent and clove-brown. Owing to its metamict condition it is isotropic in polished sections. Photoelectric-cell measurements on several polished sections give an average value for reflectivity of 19·5 % in white light, compared with a galena standard, taken as 43·8 % (S. H. U. Bowie, Geological Survey of Great Britain). The colour of fresh surfaces and the streak are grey-black and the lustre submetallic and shining. Slightly oxidized surfaces, such as crystal faces, are usually dark brown, but sometimes reddish. The crushed material is just attracted by a powerful hand-magnet. Tests with the Frantz isodynamic separator show its susceptibility to fall within the ilmenite range and to be rather less than that of haematite. The principal elements, uranium, titanium, and iron, are readily demonstrated by the usual tests. The mineral is attacked with difficulty by hydrochloric and nitric acids.

Chemical analysis.—In view of considerable discrepancies amongst early chemical analyses of this mineral (table I, nos. 2–7) it was decided to obtain a complete analysis of a carefully selected sample. Although hand-specimens may look perfectly pure, polished sections under the

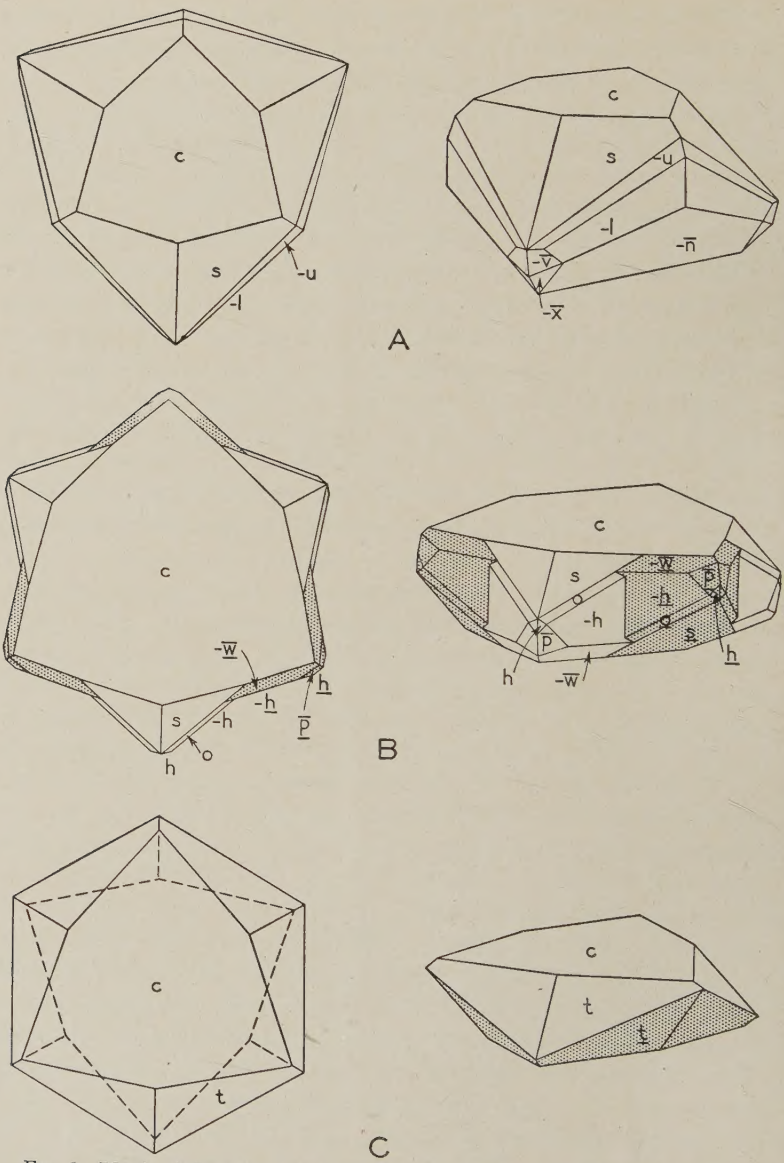

FIG. 1. Idealized drawings of (*A*) an untwinned crystal; (*B*) interpenetrant and (*C*) aggregate rotation twins about [11$\bar{2}$0]. One individual of each twin is stippled. The forms shown are *c* (0001), *h* (21$\bar{3}$0), $-h$ (12$\bar{3}$0), $-l$ (25$\bar{7}$0), $-\tilde{n}$ (03$\bar{3}$4), *o* (11$\bar{2}$1), $\tilde{p}$ (22$\bar{4}$1), *s* (52$\bar{7}$8), *t* (41$\bar{5}$6), $-u$ (34$\bar{7}$3), $-\tilde{v}$ (34$\bar{7}$2), $-\tilde{w}$ (12$\bar{3}$3), $-\tilde{x}$ (26$\bar{8}$9). The specimens on which the drawings are based are illustrated in figs. 2, 3, and 4.

microscope are usually found to contain small amounts of other minerals. After several trials, however, a polished section was prepared almost

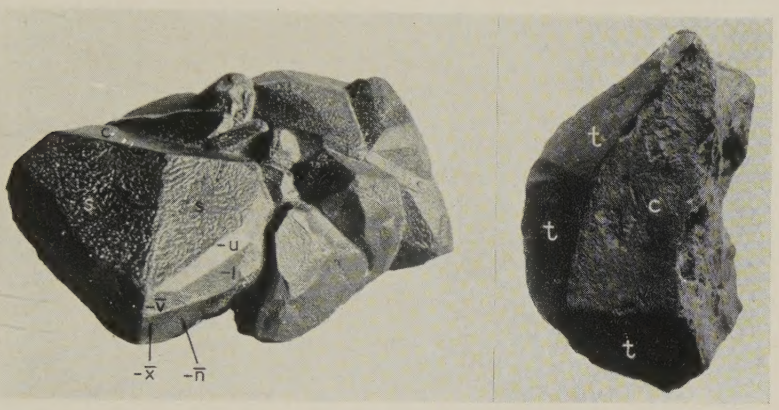

FIG. 2. Radioactive mineral from Tete, Mozambique. $\times\frac{6}{5}$. Cluster of naturally etched crystals of which the largest is untwinned. The forms shown are *c* (0001), $-l$ (25$\bar{7}$0), $-\bar{n}$ (03$\bar{3}$4), *s* (52$\bar{7}$8), *u* (34$\bar{7}$3), $-\bar{v}$ (34$\bar{7}\bar{2}$), $-\bar{x}$ (26$\bar{8}\bar{9}$). (Cf. fig. 1 A.)

FIG. 3. Radioactive mineral from Tete, Mozambique. $\times\frac{4}{3}$. Portion of an aggregate twin showing apparent holohedral symmetry. The forms shown are *c* (0001), *t* (41$\bar{5}$6). (Cf. fig. 1 C.)

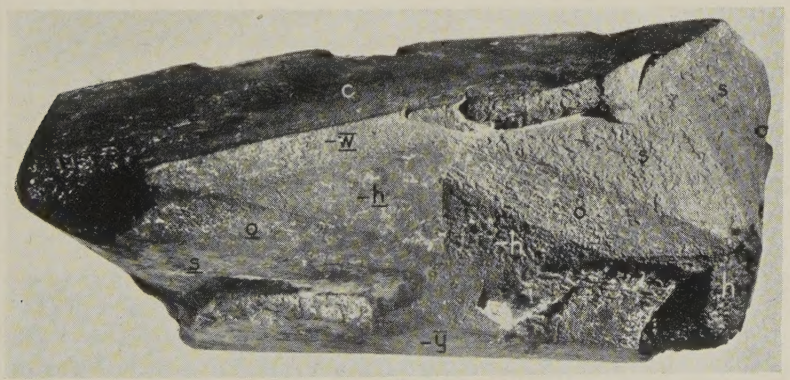

FIG. 4. Radioactive mineral from Tete, Mozambique. $\times\frac{2}{5}$. Portion of a large interpenetrant twin 12 inches long and weighing 22 pounds. The forms shown are *c* (0001), *h* (21$\bar{3}$0), $-h$ (12$\bar{3}$0), *o* (11$\bar{2}$1), *s* (52$\bar{7}$8), $-\bar{w}$ (12$\bar{3}\bar{3}$), $-\bar{y}$ (13$\bar{4}\bar{4}$). (Cf. fig. 1 B.)

entirely free from traces of impurity even at a high magnification; fortunately, the same degree of purity was still found when the section was remounted the other way up. After the bakelite had been carefully

TABLE I. Chemical analyses of the Tete mineral and davidite.

	1.	2.	3.	4.	5.	6.	7.	8.
TiO_2	54·5	51·00	60·5	36·70	47·40	45·80	51·30	54·3
Fe_2O_3	10·2	13·57	—	—	—	—	—	13·0
Cr_2O_3	0·17	3·23	4·8	3·42	4·62	4·21	4·86	
V_2O_5	1·4	—	—	0·25	0·25	0·25	0·25	4·6
U_3O_8	9·8	7·10	7·5	5·50	7·85	8·00	8·02	
FeO	16·5	12·37	27·0	21·90	23·20	22·40	24·90	16·0
ZrO_2	0·4	3·30	—	—	—	—	—	—
$(Ce, \&c.)_2O_3$ ...	5·6	n.d.	—	3·10	3·60	4·52	4·24	8·3
Na_2O	0·15	1·72	—	—	—	—	—	—
CaO	0·3	1·00	—	12·40	5·00	4·60	3·00	1·5
ThO_2	0·07	—	—	0·12	0·14	0·14	0·12	—
PbO	0·72	—	—	—	—	—	—	1·1
H_2O+ ...	0·05	1·09	—	—	—	—	—	1·5
Insol.	—	—	—	2·90	5·20	3·00	1·40	—
	99·92	99·95	99·8	86·29	97·26	92·92	98·09	100·9

1. Radioactive mineral from Tete, Mozambique; sp. gr. 4·46. The uranium was reported as UO_3 and alkali metals as Na_2O. Also contains SiO_2 0·06 %; MgO, Nb_2O_5, and Ta_2O_5 not found. Analysed by W. Ryan and P. J. Maple, Chemical Research Laboratory, Teddington, Middlesex.

2. Same; sp. gr. 4·48; also contains SiO_2 0·68, Al_2O_3 4·24, K_2O 0·32, BaO trace, MnO trace, NiO 0·05, S 0·09, H_2O- 0·19 %; analysed by E. Golding, Geological Survey of Southern Rhodesia (private communication, 1947).

3–7. Same; samples containing varying amounts of accessory minerals (see p. 105). MgO and H_2O are present but have not been determined; Nb_2O_5 and Ta_2O_5 both $< 0·5$ %. Analysed by Messrs. Johnson, Matthey & Co., London, 1947, through the courtesy of The British South Africa Company, Limited.

8. Davidite, Olary, South Australia. Also MgO 0·6 %, CuO trace; U_3O_8, Cr_2O_3, V_2O_5 4·6 %, mainly uranium oxide; very little ThO_2 in rare-earths; scandium present (according to Sir William Crookes); ZrO_2 absent. Analysed by W. T. Cooke, Chemical notes on davidite. Trans. Roy. Soc. South Australia, 1916, vol. 40, p. 267. [M.A. **1**–79.]

removed from cracks the sample was accordingly submitted to the Chemical Research Laboratory, Teddington, for analysis.

It will be seen that there are few differences between analysis 1 of the Tete mineral and analysis 8 of davidite, the chief being that the Tete mineral has more uranium and less rare-earths. When the figure of UO_3 9·8 %, analysis 1, is re-expressed as U_3O_8 9·6 % with corresponding changes in the FeO/Fe_2O_3 ratio, i.e. with Fe_2O_3 12·0, FeO 14·9 %, the similarity to the composition of davidite becomes more apparent.

An attempt has been made to derive a formula from analysis 1, though in the absence of unit-cell dimensions it must be emphasized that this is strictly provisional. Uranium has been reckoned as U^{6+} and vanadium as V^{3+}, the Fe^{3+}/Fe^{2+} ratio being adjusted accordingly. The rare-earth

oxides have been treated as Ce_2O_3. The lead is assumed to be radiogenic[1] and has been added to the uranium ratio. The ionic radius of 0·76 Å. for U^{6+} is a mean figure obtained from a paper by Samson and Sillén on the structure of barium uranate,[2] which gives U–O distances in the distorted UO_6 octahedron as 1·90, 2·12, and 2·22 Å.

	Radius.	Ionic ratios.	For 7 anions.	
Si^{4+} ...	0·39 Å.	0·00100	0·004	} 3·001
Ti^{4+} ...	0·64	0·68210	2·382	
Cr^{4+} ...	0·64	0·00224	0·008	
V^{3+} ...	0·65	0·01540	0·054	
Fe^{3+} ...	0·67	0·15854	0·553	
U^{6+} ...	0·76	0·03750	0·131	} 0·992
Fe^{2+} ...	0·83	0·19884	0·694	
Zr^{4+} ...	0·87	0·00325	0·011	
Na^{+} ...	0·98	0·00484	0·017	
Ca^{2+} ...	1·06	0·00535	0·019	
Th^{4+} ...	1·10	0·00027	0·001	
Ce^{3+}, &c.	0·99–1·18	0·03410	0·119	
OH^{-} ...	1·32	0·00555	0·019	} 7·000
O^{2-} ...	1·32	1·99851	6·981	

Grouping similarly sized ions together, it will be seen that the analysis corresponds to the empirical formula $AB_3(O,OH)_7$, where $A = Fe^{2+}$, (Ce^{3+}, &c.), U^{6+}, Ca^{2+}, Na^{+}, Zr^{4+}, Th^{4+}, and $B = Ti^{4+}$, Fe^{3+}, V^{3+}, Cr^{3+}. The ideal end-member on this tentative interpretation is thus $FeTi_3O_7$ or $FeO.3TiO_2$. Broadly speaking, replacement of Fe^{2+} by U^{6+} and rare-earths is balanced by replacement of Ti^{4+} by Fe^{3+} and V^{3+}.

The analysis of davidite may be interpreted in a similar way. V_2O_5 and U_3O_8, reported together in the analysis, have been arbitrarily assigned values of 1·4 and 3·2 % respectively.

	Radius.	Ionic ratios.	For 7 anions.	
Ti^{4+} ...	0·64 Å.	0·67960	2·267	} 2·939
V^{3+} ...	0·65	0·01540	0·051	
Fe^{3+} ...	0·67	0·18600	0·621	
U^{6+} ...	0·76	0·01636	0·055	} 1·027
Mg^{2+} ...	0·78	0·01490	0·050	
Fe^{2+} ...	0·83	0·19948	0·666	
Ca^{2+} ...	1·06	0·02675	0·089	
Ce^{3+}, &c.	0·99–1·18	0·05062	0·167	
OH^{-} ...	1·32	0·08324	0·278	} 7·000
O^{2-} ...	1·32	2·01552	6·722	

[1] On this assumption the age is estimated to be about 565 million years, in agreement with the geological age of the deposit, which is pre-Karroo and probably pre-Cambrian.

[2] S. Samson and L. G. Sillén, Die Kristallstruktur des Bariumuranates. Nicht-existenz der UO_4-Gruppe. Arkiv Kemi, Min. Geol., 1948, vol. 25A, no. 21. (M.A. **10**–539.)

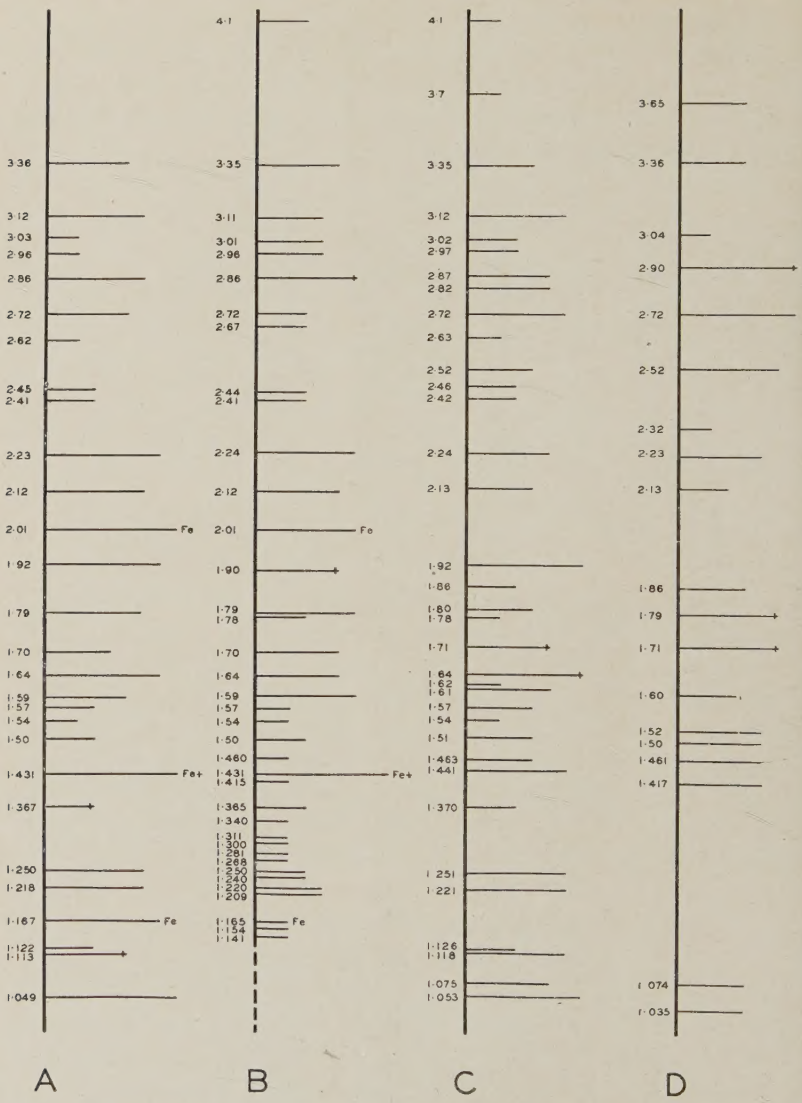

FIG. 5. Spacing-intensity plots of X-ray powder photographs of the Tete mineral after heating: (*A*) in hydrogen at 1200° C., (*B*) in nitrogen at 1200° C., (*C*) in nitrogen at 1000° C., and of davidite (*D*) in nitrogen at 1000° C.

The *d*-spacings are plotted on a logarithmic scale and their approximate values in Ångström units are given against each line, the length of which is an indication of the intensity. Lines marked 'Fe' are attributed to α-iron. A cross-bar indicates a broad line on the photograph.

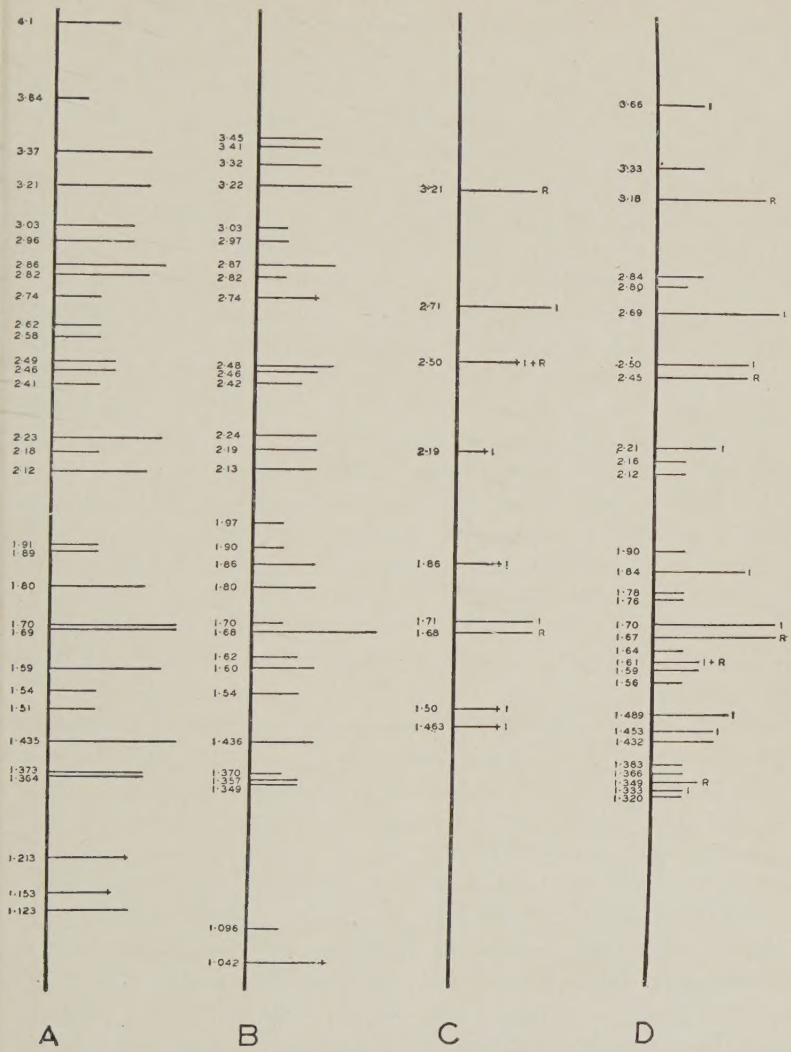

FIG. 6. Spacing-intensity plots of X-ray powder photographs of the Tete mineral (*A*) and davidite (*B*) after heating in air at 1000° C., and of sefströmite before (*C*) and after heating (*D*) in nitrogen at 1000° C. Lines marked I and R are attributed to ilmenite and rutile respectively.

All the X-ray photographs represented in figs. 5 and 6 were taken in a cylindrical camera, diameter 6 cm. with Co-$K\alpha$ radiation, λ 1·7902 Å.

Thus the available data are not inconsistent with davidite also having a formula of the type $AB_3(O,OH)_7$.

Attempts were made to synthesize the double oxides $FeO.2TiO_2$, $FeO.3TiO_2$, and $FeO.4TiO_2$ by heating the appropriate mixtures of ferrous ammonium sulphate and titanium oxide in nitrogen at 1000° C. X-ray powder patterns of the products thus obtained, however, show them to be mixtures of ilmenite and rutile in varying proportions, and quite different from the patterns of davidite and the Tete mineral heated under the same conditions.

Heat-treatment and X-ray investigations (F. A. B.).—Both davidite and the chemically similar mineral from Tete, Mozambique, are metamict, but they can be recrystallized by powdering and then heating to a high temperature for several hours. Initially the two minerals were heated for 24 hours at 1000° C. in air. Powder photographs taken subsequent to cooling, shown diagrammatically in figs. 6 A and B, are similar, and as the chemical analyses then available (table I, nos. 2 and 8) showed no essential differences the mineral from Tete was provisionally identified as davidite. It was soon realized, however, that heating in air would oxidize the ferrous iron content and perhaps result in a misleading similarity of the powder patterns. Heat-treatment in a neutral atmosphere and the subsequent X-ray study of the products will now be summarized.

It was soon discovered that the moisture content of commercial nitrogen is sufficient at high temperatures to oxidize the powdered minerals. This was obviated by passing the gas over heated iron-wool loosely packed into the first four inches of the tubular furnace. The iron-wool plug was renewed before each run and inspected at the end of each run after the furnace had been allowed to cool with the nitrogen stream still passing through. Only when the iron-wool plug retained an untarnished inner end at least one inch long was the run regarded as satisfactory. An additional check on the absence of oxygen in the neighbourhood of the heated samples was afforded by placing powdered ilmenite in the furnace close to and immediately preceding the mineral under investigation, and subsequently examining its X-ray photograph for the lines of pseudobrookite.[1]

[1] Ilmenites (B.M. 90156) from Ingelsberg, Salzburg, and (B.M. 37302) from Ilmen Mts., Russia, when heated in air for 24 hours at 1000° C. yield patterns identical with that of pseudobrookite (B.M. 74455) from Arany, Transylvania, the probable reaction being $2FeTiO_3 + O \rightarrow Fe_2TiO_5 + TiO_2$; no lines due to rutile, anatase, or brookite in addition to those of pseudobrookite, have, however, been detected on powder photographs of oxidized ilmenite.

Figs. 5 C and D show in diagrammatic form the X-ray patterns of powdered specimens of the Tete mineral and of davidite obtained as just described after heating to 1000° C. in a completely neutral atmosphere. They differ from the air-heated patterns represented in figs. 6 A and B, as was to be expected. There are also differences between the two nitrogen-heated patterns (figs. 5 C and D) which cannot be disregarded. It should be emphasized at this point that many samples of the Tete mineral taken from specimens with and without crystal faces have been examined and always yield the same pattern after heat-treatment under the same conditions. This can only be so if the mineral in its metamict condition has a uniform composition throughout and on recrystallization yields either one phase or a mixture of phases always in the same proportions.

It was decided at this stage to raise the temperature of heat-treatment and also to investigate patterns obtained by heating in a reducing as well as a neutral atmosphere. When the Tete mineral was heated to 1200° C. in nitrogen a different pattern was obtained, three lines of which can be attributed to α-iron, showing that the mineral dissociates at the higher temperature (fig. 5 B). X-ray photographs were also taken of the Tete mineral after heating in hydrogen at 800°, 1000°, and 1200° C. respectively. The patterns obtained for all three temperatures are essentially the same (fig. 5 A) excepting that the lines are sharper and more numerous for the higher temperatures, indicating better crystallization; α-iron lines occur in all these photographs. Apart from this identification of α-iron in the Tete mineral after heating in hydrogen or in nitrogen at 1200° C. no other phases have been recognized on any of the X-ray photographs. Rutile, brookite, anatase, haematite, magnetite, ilmenite, and pseudobrookite have been looked for without success. This suggests that the Olary and Tete minerals crystallize as single-phase systems, not mixtures, when heated in nitrogen at 1000° C., but unfortunately it has not proved possible to index the powder photographs, using Bunn's charts.[1]

It was natural to hope that as the shapes of the Tete crystals conform to trigonal symmetry it would be possible to index the powder pattern of the recrystallized mineral on the basis of a unit cell with the same symmetry and with an axial ratio simply related to that obtained from rough measurements of interfacial angles, viz. 1:1·37 (page 102). This cannot be done, neither has it proved possible to index any of the powder photographs of the Tete mineral or davidite assuming trigonal, hexa-

[1] C. W. Bunn, Chemical crystallography, Oxford, 1945, p. 132. [M.A. 9 217.]

gonal, tetragonal, or cubic symmetry. This may be due to lower symmetry or large unit-cell dimensions; or, of course, to the presence of more than one substance in the recrystallized mineral.

To sum up, there are real, though unexplained, differences in the X-ray powder photographs given by davidite and the Tete mineral after heat-treatment. On this evidence alone, however, it does not seem warrantable to claim that the radioactive mineral from Tete, Mozambique, is a new and distinct species. It should rather be classified as a variety of davidite until unambiguous evidence to the contrary is forthcoming. Davidite itself should be reinstated as a true species, although it may prove difficult ever to decide what its symmetry and crystal structure were before it became metamict.

Sefströmite. -This name[1] was applied (apparently by Sir Douglas Mawson, though not published by him) to a supposed vanadiferous variety of ilmenite occurring with davidite at Radium Hill, near Olary, South Australia. Specimens in the British Museum collection since 1907 (reg. no. 1907,1027 and 1028) yield before heat-treatment lines due to rutile as well as ilmenite (fig. 6 c). After heating in nitrogen to 1000° C. a much stronger and more line-rich pattern (fig. 6 d) was obtained, showing a few weak lines additional to those of rutile and ilmenite. Sefströmite is, therefore, a mixture of one or more metamict minerals, not, however, davidite itself, with rutile and ilmenite.

In conclusion we should like to record our thanks to the Director of the Chemical Research Laboratory, Teddington, for the chemical analysis by Mr. W. Ryan and Miss P. J. Maple, and to Dr. M. H. Hey, who gave us much helpful advice during the progress of the work.

[1] T. Crook, Min. Mag., 1910, vol. 15, p. 281; L. J. Spencer, tom. cit., p. 431.

The optical properties and composition of the acmitic pyroxenes.

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[Read January 26, 1950.]

THE occurrence of acmitic pyroxenes in the post-Cambrian intrusions of the north-west of Scotland was first noted by Teall (Horne and Teall, 1892) who recorded aegirine in two dikes discovered by Gunn in the Coigach district of Ross-shire, and aegirine-augite in the borolanite of the Cnoc-na-Sròine mass. Since then, acmitic pyroxenes have been recorded by Teall (1900) from the Assynt felsites, Shand (1910) from dikes of the border zone of Cnoc-na-Sròine, and Phemister (1926) from the dikes and plutonic rocks of the Loch Ailsh laccolite.

Having undertaken a comprehensive examination, in the field and in the laboratory, of the post-Cambrian sills and dikes of the Assynt district, the writer determined some of the optical constants of the acmitic pyroxenes of these intrusions. Arising from this work the considerable data now available on the acmitic pyroxenes has been reviewed. A chemical analysis has also been carried out, and it is hoped that the information assembled and re-interpreted here may be of some general interest.

The name *acmite* (Achmit) was proposed by Berzelius for crystals described by Ström from the parish of Eger in southern Norway (Ström, 1821) and alluded to their pointed shape. *Aegirine* (Aegirin) was the name given by Esmark to a mineral occurring on an island in the sea in the neighbourhood of Skansfjord, and was so called after the Scandinavian sea-god Aegir (Berzelius, 1835).

Aegirine is found as greenish-black crystals having blunt terminations, acmite as pointed brown crystals. Under the microscope aegirine is of green colour and is strongly pleochroic, whilst acmite is usually brown in colour and is only weakly pleochroic. The two species were shown to be essentially the same, $NaFe^{+3}Si_2O_6$, by Tschermak in 1872, but the two names still persist. The term 'acmite' is also used for the theoretical $NaFe^{+3}Si_2O_6$ molecule. The name aegirine-augite was suggested by

[1] Communicated with the permission of the Director.

Rosenbusch (Aegirin-Augit) in 1892 for minerals intermediate between aegirine and augite and has been widely used for the green sodic pyroxene of high extinction angle.

Aegirine from the Assynt district, Sutherlandshire.

The aegirine here described occurs in an aegirine-nepheline-syenite pegmatite dike cutting the ultrabasic rock of the Cnoc-na-Sròine mass. The dike, which is a member of the great post-Cambrian sill and dike suite of Assynt, outcrops in the Bad na h'Achlaise 700 yards south of Ledmore. It is about 5 feet 6 inches thick and is collinear with a 2-foot dike of variable nepheline-syenite in the adjoining Cambrian quartzite. Dr. J. Phemister (Macgregor and Phemister, 1937) has pointed out that this suggests that the pyroxenite is intrusive in Cambrian quartzite, and not in limestone as thought by Shand (1910).

Petrologically, the dike-rock is of variable composition. Parallel, half-inch-long prisms of aegirine occur in narrow streaks set in coarsely crystalline grey felspar with pink micaceous pseudomorphs representing original euhedral nepheline. In thin section (Geological Survey slice no. S. 37399) the felspar is seen to be predominantly of perthite akin to soda-orthoclase and containing only a little albite. Chequer-albite forms selvedges along the margins of the felspar crystals. The nepheline is now represented by pinitic mica. Scarce magnetite crystals are present, moulded upon felspar, and there are occasional anhedra of biotite. Euhedral aegirine, which occurs in both the felspar and in the nepheline pseudomorphs, in places has a fairly robust habit, yet elsewhere forms slender prisms.

To separate the aegirine the rock was crushed to pass a 50 mesh sieve and then separated in methylene iodide. The heavy fraction, consisting almost entirely of aegirine, was passed through a Frantz isodynamic separator and finally the sample was hand picked. The chemical analysis and optical properties of the mineral are given in table I.

It may be noted that if $H_2O(+105^\circ C.)$ is excluded the analysis may be expressed as $(Na,Ca,K)_{1\cdot007}(Fe^{+3},V,Ti,Fe^{+2},Mn,Mg,Al)_{1\cdot009}(Si,Al)_{2\cdot000}O_{6\cdot000}$, which corresponds very closely with the ideal formula $XYSi_2O_6$, and perhaps indicates that the water is not really constitutional. The weight percentage of the 'acmite' molecule present is 73·4.

The refractive indices of the mineral were determined by the immersion method and the optic axial angle on a universal stage. The pleochroism is α deep green, β deep green, γ yellowish-brown, and the absorption $\alpha > \beta = \gamma$. Owing to the high refractive indices, intense

TABLE I. Analysis of aegirine from Assynt, Sutherland.

		Number of atoms when (O + OH) = 6					
SiO_2	51·35	Si^{+4}	1·961			2·000	
Al_2O_3	2·88*			0·039			
Fe_2O_3	25·43	Al^{+3}	0·129				
FeO	3·70			0·090			
MgO	0·58	Fe^{+3}	0·728		0·994		1·997
CaO	3·29	V^{+3}	0·001				
Na_2O	11·65	Ti^{+4}	0·018				
K_2O	0·14	Mg^{+2}	0·033				
$H_2O-105°$ C.	0·09†	Mn^{+2}	0·006				
$H_2O+105°$ C.	0·24†	Fe^{+2}	0·118				
TiO_2	0·65						
MnO	0·18	Na^{+1}	0·861		1·003		
V_2O_3	0·02	Ca^{+2}	0·135				
ZrO_2	not detected	K^{+1}	0·007				
$(Ce,Yt)_2O_3$	,, ,,						
		OH^{-1}	0·061		6·000		
	100·20	O^{-2}	5·939				

Analysis by Geochemical Laboratories, Wembley.

* Corrected for V_2O_3.

† Determined in the Chemical Laboratory, Geological Survey and Museum.

α 1·751, β 1·786, γ 1·800, $2V_\alpha$ 65–73°, $\alpha : c = 1°$.

A quantitative spectroscopic determination carried out by Dr. J. A. C. McClelland of the Government Laboratory showed V_2O_3 0·02–0·03 % and the Al_2O_3 figure has been corrected accordingly.

colour, and moderate to strong dispersion the determination of the optic axial angle was attended by considerable difficulty, and a single value has not therefore been quoted. The range of figures determined was 65–73° and the mean 68½°, but as it is not possible to appraise the errors, this figure should be regarded with caution.

Structure and composition.

The structure of acmite was studied by Warren and Briscoe (1931) who showed that it had the same structure as the other monoclinic pyroxenes, typified by diopside, and consisted of chains of silicon–oxygen tetrahedra linked by the cations Na^{+1} and Fe^{+3} in 8-fold and 6-fold co-ordination respectively. They gave the general formula for the monoclinic pyroxenes $X_mY_{2-m}(Si,Al)_2(O,OH,F)_6$, where m tends to be 1·0 or 0, X = Na,Ca,K,Mn, and Y = Mg,Fe,Al,Ti,Mn.

In the past, attempts to display the variation of physical properties with chemical composition of the acmitic pyroxenes have mainly been based upon interpretations of analyses in terms of theoretical oxides, or 'minals' as they have been termed by Alling (1921). Winchell (1933) presented a double triangular diagram to show the optical properties of

the pyroxenes, plotting diopside and hedenbergite as the ends of the common side of the triangles and acmite and jadeite as the two vertices. He remarked, however, that the diagram was based upon insufficient data and was therefore not accurate. An additional reason for the inaccuracy lies, in the opinion of the writer, in the variable chemical composition of the minerals themselves. Larsen (1942) published a graph showing the various optical properties of the åcmitic pyroxenes plotted against Fe_2O_3 content, with an interpolated scale of acmite. He did not give the sources of the figures he used. Ostrovsky (1946) has given data for synthetic aegirine-diopside mixtures.

In table II are shown the calculated percentages of acmite, hedenbergite, and diopside for thirteen minerals quoted by Washington and Merwin (1927) together with the sum of the remaining constituents in each mineral.

Table II. Calculated percentages of acmite, hedenbergite, diopside, and remaining constituents in thirteen analysed specimens.

No.	Acmite, $NaFeSi_2O_6$.	Hedenbergite, $CaFeSi_2O_6$.	Diopside, $CaMgSi_2O_6$.	Remaining constituents.
1.	89·17	2·48	0	8·35
2.*	86·36	7·19	0	6·55
3.	82·70	1·24	0	16·06
4.	82·70	5·71	0	11·59
5.	81·31	7·19	0	11·50
6.	73·46	9·67	8·64	8·23
7.	67·91	18·35	6·70	7·04
8.	65·60	15·87	9·07	9·46
9.	65·60	19·09	1·08	14·23
10.	62·83	7·19	14·90	15·08
11.	55·44	23·81	12·31	8·44
12.	36·04	14·13	34·78	15·05
13.	9·70	59·77	17·28	13·25

* Calculated from rock analysis by Washington and Merwin.

1, Quincy, Mass., U.S.A. 2, Rockall Island. 3, Rundemyr, Norway. 4, Kangerdluarsuk, Greenland. 5, 'Brevik', Norway. 6, Låven, Langesund Fjord, Norway, 7–8, Magnet Cove, Ark., U.S.A. 9, Arö Skjär, Norway. 10, Libby, Mont., U.S.A. 11, Låven, Langesund Fjord, Norway. 12, Libby, Mont., U.S.A. 13, Salem Neck. Mass., U.S.A.

In calculating the composition in terms of acmite, hedenbergite, and diopside, these authors allotted firstly the greatest possible percentage of Na_2O and Fe_2O_3 to form acmite. Hedenbergite and diopside were then calculated. If FeO+MgO+(MnO) was in excess of CaO an arbitrary choice had then to be made. Washington and Merwin gave preference to FeO, first calculating as much hedenbergite as possible and then assigning the remaining CaO to MgO to form diopside. This proce-

TABLE III. Atomic proportions of analysed acmitic pyroxenes.

No.	Si.	Al.	[Al].	Ti.	Fe^{+3}	Mg.	Fe^{+2}	Mn^{+2}	Ca.
1.	1·989	0·045	0·034	0·017	0·911	0·008	0·029	0·011	0·023
2.	1·959	none	none	0·022	0·893	0·016	0·059	0·009	0·070
3.	2·003	0·094	0·094	0·028	0·835	0·020	0·007	0·005	0·012
4.	1·968	0·080	0·048	0·007	0·833	0·020	0·099	0·010	0·054
5.	1·995	0·060	0·055	0·016	0·811	0·025	0·070	0·003	0·065
6.	1·977	0·044	0·021	0·016	0·773	0·125	0·086	0·003	0·179
7.	1·957	0·082	0·039	0·003	0·682	0·086	0·170	0·003	0·246
8.	1·969	0·050	0·019	0·057	0·647	0·129	0·136	0·008	0·242
10.	1·976	0·017	none	0·025	0·622	0·176	0·047	0·019	0·226
11.	1·944	0·126	0·070	0·015	0·550	0·131	0·219	0·016	0·350
12.	2·115	0·065	0·065	0·011	0·368	0·042	0·122	0·015	0·518
13.	1·886	0·207	0·093	0·041	0·100	0·186	0·564	none	0·755
14.	1·989	0·071	0·060	0·037	0·754	0·081	0·076	0·007	0·106
15.	1·982	0·146	0·129	0·010	0·840	0·039	0·020	none	0·007
16.	1·913	0·192	0·105	0·023	0·345	0·220	0·316	0·013	0·548
17.	2·052	0·057	0·057	0·073	0·630	0·022	0·051	0·014	0·212
18.	2·02	0·17	0·17	0·002	0·77	0·01	0·02	0·01	0·03
19.	1·923	0·099	0·022	0·010	0·400	0·304	0·238	0·020	0·548
20.	1·961	0·129	0·090	0·018	0·728	0·033	0·118	0·006	0·135

No.	Na.	K.	Zr.	V.
1.	0·868	0·018	0·008	n.d.
2.	0·884	none	0·052	n.d.
3.	0·952	0·009	0·004	n.d.
4.	0·946	0·018	0·003	n.d.
5.	0·868	0·011	0·025	n.d.
6.	0·713	0·013	n.d.	n.d.
7.	0·739	0·012	0·002	n.d.
8.	0·688	0·004	n.d.	n.d.
10.	0·770	0·011	n.d.	0·121
11.	0·592	0·007	0·001	n.d.
12.	0·481	0·013	n.d.	0·091
13.	0·249	0·022	n.d.	n.d.
14.	0·840	0·017	0·003	n.d.
15.	0·850	0·026	n.d.	n.d.
16.	0·405	0·020	n.d.	n.d.
17.	0·764	0·009	n.d.	none
18.	0·93	0·01	n.d.	n.d.
19.	0·394	0·019	n.d.	0·001
20.	0·861	0·007	none	0·001

n.d. = not determined.

1–13. See table II for localities (Washington and Merwin, 1927).
14. Bearpaw Mountains, Mont., U.S.A. (Pecora, 1942).
15. French River, Ontario, Canada (Walker and Parsons, 1926).
16. Iron Hill, Colo., U.S.A. (Larsen, 1942).
17. Libby, Mont., U.S.A. (Goranson, 1927).
18. Norra Kärr, Sweden (Adamson, 1944) (atomic proportions given).
19. Ilmen Mountains (Zavaritzky, 1946).
20. Bad na h'Achlaise, Assynt, Sutherlandshire (new analysis).

dure they adopted because they found the hedenbergite molecule more abundant than that of diopside. Remaining constituents were then allotted to the theoretical molecules $Na_2O.Al_2O_3.4SiO_2$, $Na_2O.V_2O_3.4SiO_2$, $Na_2O.SiO_2$, $MgO.SiO_2$, $FeO.SiO_2$, $Fe_2O_3.3SiO_3$, $Al_2O_3.3SiO_2$, Al_2O_3, and SiO_2. It will be seen from the table that the sum of these various remaining constituents may amount in some cases to nearly one-sixth of the molecule, even in those minerals with high acmite content. It is in the variable quantity and composition of these remaining constituents that one of the principal causes of the variability in the optical properties appears to lie: the acmitic pyroxenes are of too complicated composition to be readily expressible in terms of the three 'end-members'.

The chemical composition may, however, be recalculated as atomic proportions. Atomic proportions for the pyroxenes studied by Washington and Merwin, together with a number based on analyses published since the date of their paper, are presented in table III. These have been calculated, as in Berman's paper (1937) on the basis $O+OH = 6$, if necessary making $Si = 2$ by utilizing a proportion of the Al present. For convenience in the sequel, the aluminium in 6-fold co-ordination, which remains after allotting the amount (in 4-fold co-ordination) necessary to make $Si = 2$, is denoted as [Al] and referred to as 'excess aluminium'. The almost exact equation, after excluding water, of the *X* and *Y* groups in the Assynt aegirine was not found to be repeated in the other analyses, and they have all therefore been computed without first excluding water (+105° C.).

The various rules governing the distribution of elements in minerals were deduced by Goldschmidt, whose results have been confirmed many times, as, for example, in the recent careful study by Nockolds and Mitchell (1948) of the trace elements of the Caledonian plutonic rocks. In the present study the association of elements of similar ionic size is clearly displayed. The mutual relationships of the various elements in the acmitic pyroxenes are best seen from the graphs (figs. 1a, b, c). The validity of the following statements is apparent:

1. Sodium and potassium together vary directly with ferric iron, titanium, excess aluminium, and vanadium (fig. 1b). If Fe^{+3} alone is plotted against $Na^{+1}+K^{+1}$ the approximation $Fe^{+3} = \Sigma Na^{+1}$ is not so good, corroborating the postulated ionic replacements.
2. Magnesium and ferrous iron together vary directly with calcium (fig. 1c).
3. Sodium and potassium together vary inversely with calcium (fig. 1a).

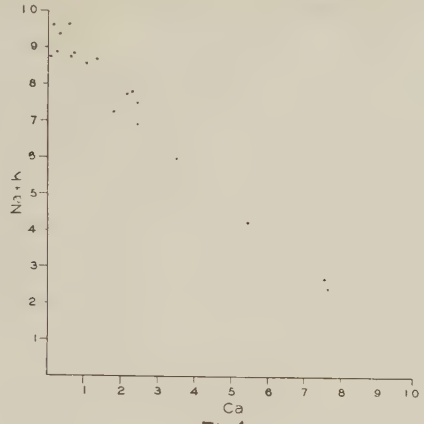

Fig.1a

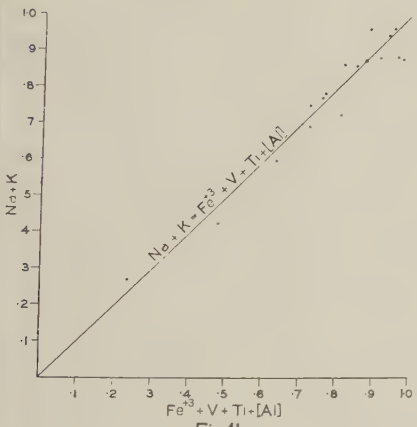

Fig.1b

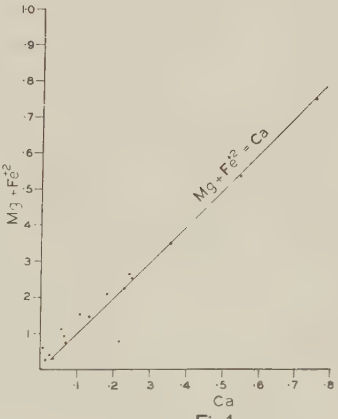

Fig.1c

FIG. 1. Graphs showing the relative atomic proportions in the acmitic pyroxenes.

TABLE IV. Ionic radii (Evans, 1939).

Si^{+4}	0·39	V^{+3}	0·65	Fe^{+2}	0·83	Na^{+1}	0·98 Å.
Al^{+3}	0·57	Fe^{+3}	0·67	Zr^{+4}	0·87	Ca^{+2}	1·06
Ti^{+4}	0·64	Mg^{+2}	0·78	Mn^{+2}	0·91	K^{+1}	1·33

The ionic radii of the elements concerned are shown in table IV. It will be seen that Fe^{+3}, V^{+3}, Ti^{+4}, and Al^{+3} are of similar size, Mg^{+2} and Fe^{+2} are of similar size, whilst Ca^{+2} is intermediate in size between Na^{+1} and K^{+1}. The introduction of the divalent calcium ion in place of

Na^{+1} immediately requires a balancing of the electrostatic charges by a concomitant introduction of a second divalent ion in place of Fe^{+3}. Since, moreover, there is a direct relationship between ΣNa^{+1} and ΣFe^{+3}, Ca^{+2} would be expected to vary directly with the sum of Mg^{+2} and Fe^{+2}.

Optical properties.

The optical properties of the acmitic pyroxenes whose atomic ratios are presented in table III are shown in table V.

TABLE V. Optical properties of the acmitic pyroxenes.

	α.	β.	γ.	2V.	$\alpha : c$.
1.	1·767	1·806	1·823	−60°	6°
2.	1·765	—	1·815	—	3–5
3.	1·770	1·811	1·825	—	3
4.	1·769	1·805	1·824	—	4
5.	1·760	1·790	1·810	—	0
7–8.	1·763	1·780	1·812	—	−3–+3
10.	1·745	1·770	1·782	−69°	1–2
11.	1·744	1·768	1·782	−70° −80°	10
12.	1·720	—	1·747	—	24
13.	1·711	1·729	1·759	+75° +80°	27–32
14.	1·757	1·786	1·797	−62°	low
15.	1·752	1·788	1·801	−63°	—
16.	1·730	1·748	1·768	90°	14
17.	1·742	1·768	1·787	−81°	2
18.	—	—	—	−58°	3
19.	1·720	1·740	1·757	−82° −88°	14–15
20.	1·751	1·786	1·800	−68½°	1
21.	1·776	1·819	1·836	−61°	8–10

1–20, as tables II III. 21, synthetic acmite (Washington and Merwin, 1927).

The relationships between the composition and optical properties have been expressed by means of a triangular diagram (fig. 2). In using triangular co-ordinates it is necessary to assume the cations to sum to 2, and the vertices have therefore been taken to denote $(Na^{+1}+K^{+1}) = 2$, $(Fe^{+3}+V^{+3}+Ti^{+4}+[Al]^{+3}) = 2$, and $(Mg^{+2}+Fe^{+2}+Zr^{+4}+Mn^{+2}+Ca^{+2}) = 2$. As the ideal summation to 2 is but rarely attained in nature each analysis appears not as point but as a small triangle. These triangles, representing the atomic proportions given in table III, are shown in fig. 2, and it will be seen that they are mainly quite small. An exception is analysis no. 12 which is not shown as the triangle is too large to permit of its use. This doubtless arises from the high Si^{+4} content (2·115) which casts doubt on the veracity of the analysis. It should be noted that in plotting the diagrams Ca has not been included with Na+K as the points would not then lie on an altitude.

To plot the optical properties the centre of each of these triangles has been taken as representing the idealized composition. All such points lie very close to the line A–B representing $\Sigma Na^{+1} = \Sigma Fe^{+3}$ and for the present purposes may be considered to lie on the line. The refractive

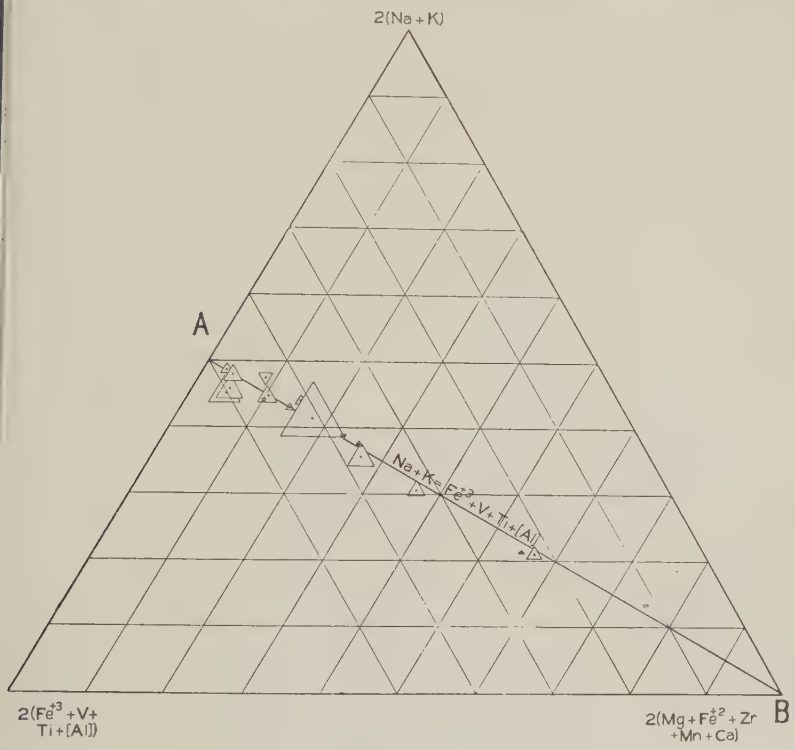

FIG. 2. The chemical composition of the acmitic pyroxenes.

indices and optic axial angle have been plotted in fig. 3 using this line as abscissa of composition so that for any given value of α, β, γ, or 2V a theoretical composition is readily obtained from the corresponding point on AB. Having obtained the theoretical composition in terms of ΣNa^{+1}, ΣMg^{+2}, and ΣFe^{+3}, the approximate content of Ca^{+2} may be obtained from fig. 1b, since Ca^{+2}, Mg^{+2}, and Fe^{+2} together constitute the majority of $(Mg^{+2}+Fe^{+2}+Zr^{+4}+Mn^{+2}+Ca^{+2})$ present.

The range of compositions shown by minerals having similar optical properties appears to arise principally from replacement of the Mg^{+2} and Fe^{+2} by each other. This cannot be detected from the optical properties

and remains a source of considerable error. Other properties of the minerals were plotted in a similar manner, but showed too great irregularities to be of much value. It may, however, be remarked that within the range of minerals now described the extinction angle varies rather

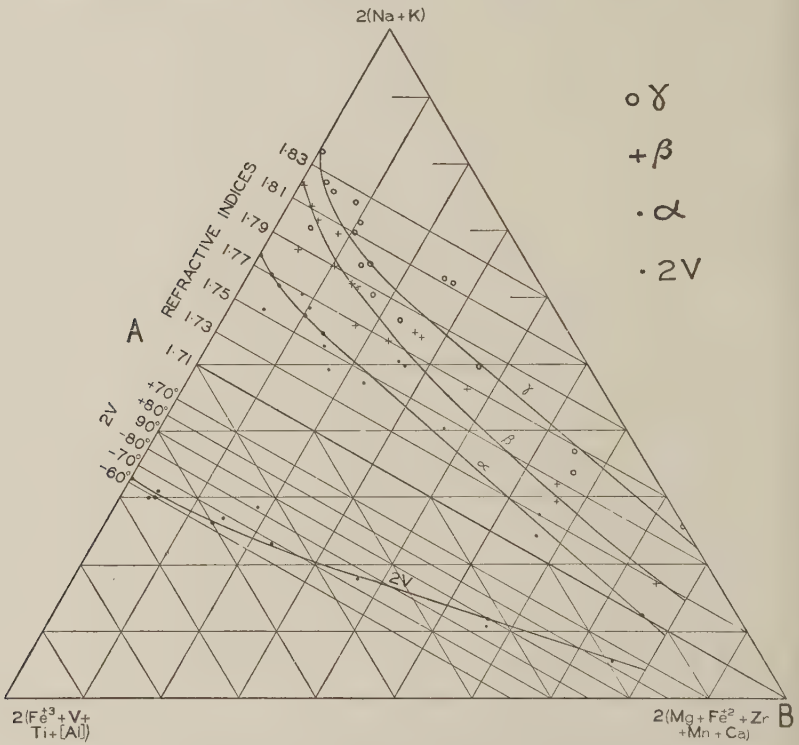

Fig. 3. The relationships of the optical properties to the chemical composition of the acmitic pyroxenes.

irregularly from 8–10° (in the obtuse angle) for pure acmite through 0° to 27–32° (in the acute angle) for aegirine-augite (acmitic-diopsidic hedenbergite) of β 1·729; the specific gravity ranges irregularly from 3·59 to 3·42 and the birefringence varies rather irregularly from 0·069 for pure acmite to 0·038 for the mineral with β 1·748.

Nomenclature.

Washington and Merwin adopted the following nomenclature. (1) Where there was present 80 % or more of one of the 'end-members', the mineral was called by the name of the end-member—acmite,

diopside, or hedenbergite. (2) If only two end-members were present such names as acmitic diopside or diopsidic acmite were used, but members intermediate between diopside and hedenbergite, with 10 % or less of acmite were called augite. (3) The terms acmitic augite or augitic acmite were applied when all three end-members were present in large amount. When first describing aegirine-augite, Rosenbusch (1892) gave the extinction ($\gamma:c$) as 55° and, comparing diopside, basaltic augite, aegirine-augite, and aegirine, gave aegirine-augite as having the extinction ($\gamma:c$) 60° and aegirine 94°. This figure for aegirine-augite corresponds roughly to a mineral containing only about $Na_{0\cdot25}Fe^{+3}_{0\cdot25}$.

The restriction by Washington and Merwin of the term 'acmite' to minerals containing 80 % of the theoretical molecule, roughly equivalent to $Na_{0\cdot8}Fe^{+3}_{0\cdot8}$, appears to the writer rather to limit the use of the name. On the other hand, limiting 'aegirine-augite' to minerals containing up to $Na_{0\cdot25}Fe^{+3}_{0\cdot25}$ also appears to be too rigid. Many minerals lie in the range between $Na_{0\cdot8}Fe^{+3}_{0\cdot8}$ and $Na_{0\cdot25}Fe^{+3}_{0\cdot25}$. It is therefore suggested that a convenient division of the aegirine–aegirine-augite series might be taken at $Na_{0\cdot45}Fe^{+3}_{0\cdot45}$, at or about which $2V = 90°$. Negative minerals would then continue to be denoted as aegirine and positive ones as aegirine-augite. This division corresponds to an extinction angle of about 15° ($\gamma:c$ 75°), the lower figure quoted by Rogers and Kerr (1933) for aegirine-augite.

It might be objected that the aegirine group proposed has rather a long range of refractive indices (β 1·744 to 1·819). The refractive indices of aegirine-augites of small acmite content, not here considered, may, however, be low. The typical mean refractive index of aegirine-augite is commonly quoted as 1·687 and within the range 1·687–1·819, the division now suggested is approximately central. The extinction angle of 15° is similarly placed. A further possible objection is that within the group, between $Na_{0\cdot45}Fe^{+3}_{0\cdot45}$ and $Na_{0\cdot50}Fe^{+3}_{0\cdot50}$ the acmite molecule would not exceed the sum of the other molecules. It is, however, very unlikely that any other single molecule would be present in greater quantity than the acmite. The advantages of the proposed division thus appear to outweigh the disadvantages, and for most acmitic pyroxenes the division affords an easy method of classification.

The two names 'aegirine' and 'aegirine-augite' are adequate for general descriptive purposes. When greater precision is required and the mineral has been analysed, the nomenclature proposed by Washington and Merwin, or better, the calculated formula may be used. 'Aegirine' is to be preferred to 'aegirite', since the mineral was first described, in

German, as 'Aegirin'. It may be remarked that although in the later editions of Dana's 'System of mineralogy' the mineral is recorded as 'ægirite' and 'aegirite', in the earlier editions in which the name first appeared (3rd edit., 1850; 4th edit., 1854) it was given as 'ægirine'.

It is suggested that in the present state of our knowledge, the choice of the name 'acmite' or 'aegirine' should depend upon the optical properties of the mineral: thus, green pleochroic varieties should be termed aegirine and brownish weakly pleochroic varieties acmite. The distinction should not, as has sometimes been the case, be based upon chemical composition.

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References.

Adamson (O. J.), 1944. The petrology of the Norra Kärr district. An occurrence of alkaline rocks in southern Sweden. Geol. För. Förh. Stockholm, vol. 66, pp. 113–255 (p. 135). [M.A. **9**–87.]

Alling (H. L.), 1921. The mineralography of the feldspars. Journ. Geol. Chicago, vol. 29, pp. 193–294. [M.A. **3**–33.]

Berman (H.), 1937. Constitution and classification of the natural silicates. Amer. Min., vol. 22, pp. 342–408.

Berzelius (J.), 1835. Neues Jahrb. Min., p. 184.

Evans (R. C.), 1939. An introduction to crystal chemistry. Cambridge. [M.A. **7**–311.]

Goranson (R. W.), 1927. Aegirite from Libby, Montana. Amer. Min., vol. 12, pp. 37–39. [M.A. **3**–455.]

Horne (J.) and Teall (J. J. H.), 1892. On borolanite—an igneous rock intrusive in the Cambrian limestone of Assynt, Sutherlandshire, and the Torridon sandstone of Ross-shire. Trans. Roy. Soc. Edinburgh, vol. 37, pp. 163–178.

Larsen (E. S.), 1942. Alkalic rocks of Iron Hill, Gunnison County, Colorado. Prof. Paper, U.S. Geol. Surv., 197–A. [M.A. **9**–174.]

Macgregor (M.) and Phemister (J.), 1937. Geological excursion guide to the Assynt district of Sutherland. Edinburgh Geol. Soc., 1937.

Nockolds (S. R.) and Mitchell (R. L.), 1948. The geochemistry of some Caledonian plutonic rocks: a study in the relationship between the major and trace elements of igneous rocks and their minerals. Trans. Roy. Soc. Edinburgh, vol. 61, pp. 533–575. [M.A. **10**–424.]

[Ostrovsky (I. A.)] Островский (И. А.), 1946. Оптические свойства синтетических эгирин-диопсидов. [Optical properties of synthetic aegirine-diopsides.] Д. С. Белянкин, Акад. Наук СССР. [D. S. Belyankin Jubilee vol., Acad. Sci. U.S.S.R.], pp. 505–512. [M.A. **10**–464.]

Pecora (W. T.), 1942. Nepheline syenite pegmatites, Rocky Boy stock, Bearpaw Mountains, Montana. Amer. Min., vol. 27, pp. 397–424. [M.A. **9**–173.]

PHEMISTER (J.), 1926. Strath Oykell and Lower Loch Shin. Mem. Geol. Surv.

ROGERS (A. F.) and KERR (P. F.), 1933. Thin-section mineralogy. New York. [M.A. **5**–433.]

ROSENBUSCH (H.), 1892. Mikrosk. Physiogr., vol. 1, p. 537.

SHAND (S. J.), 1910. On borolanite and its associates in Assynt. Trans. Edinburgh Geol. Soc., vol. 9, pp. 376–416.

STRÖM (P.), 1821. Undersökning af ett nytt fossil. K. Vet. Acad. Handl. Stockholm, p. 160; BERZELIUS (J.), ibid., p. 163.

TEALL (J. J. H.), 1900. Nepheline-syenite and its associates in the north-west of Scotland. Geol. Mag., dec. 4, vol. 7, pp. 385–392.

TSCHERMAK (G.), 1872. Ueber Pyroxen und Amphibol. Min. Mitt., for 1871, p. 17 (also in Jahrb. Geol. Reichsanstalt, Wien, 1872, vol. 21, for 1871).

WALKER (T. L.) and PARSONS (A. L.), 1926. Minerals from the nepheline syenite area, French river, Ontario. Univ. Toronto Studies, Geol. Ser., no. 22, pp. 5–14. [M.A. **3**–302.]

WARREN (B. E.) and BISCOE (J.), 1931. The crystal structure of the monoclinic pyroxenes. Zeits. Krist., vol. 80, pp. 391–401. [M.A. **5**–186.]

WASHINGTON (H. S.) and MERWIN (H. E.), 1927. The acmitic pyroxenes. Amer. Min., vol. 12, pp. 233–252. [M.A. **3**–374.]

WINCHELL (A. N.), 1933. Elements of optical mineralogy, vol. 2, p. 223. [M.A. **5**–337.]

[ZAVARITZKY (A. N.)] Заварицкий (А. Н.), 1946. Интересный пример сиенит-пегматита из Ильменских гор. [An interesting example of a syenite-pegmatite from Ilmen Mountains.] Вопросы минералогии, геохимии, и петрографии. [Problems in mineralogy, geochemistry, and petrography. Fersman memorial volume], Moscow and Leningrad (Acad. Sci. U.S.S.R.), pp. 319–325. [M.A. **10**–433.]

Calc-silicate skarn veins in the limestone of Lough Anure, Co. Donegal.

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Introduction.

A REMARKABLE series of wollastonite-garnet-idocrase veins occurs in the limestone quarries of Lough Anure in the Thorr area of Donegal. This locality lies on the extreme south of the one-inch Geological Survey of Ireland Sheet no. 9, and on the six-inch O.S. Sheet no. 41. S.E. In this area large isolated relics of Dalradian sediments are surrounded by a quartz-diorite which is highly modified at the contacts. This complex is intruded by an alkali-granite. The relict masses may be roof pendants or enclosures, and they are certainly structurally related to one another. It is the purpose of the present paper to describe the mineralization of one particular set of veins in a limestone forming part of one of the masses and exposed in two quarries about 300 yards SW. of the Lough Anure Technical School.

The area was surveyed by the Irish Geological Survey during the years previous to 1889, the mineralogy being recorded in the Memoir to Sheet 9 (1). Previous to this official survey, the main mineralogical contribution was that of Scott (2). In these and other works many references are made to calc-silicate minerals, but no details are given of the type of wollastonite-idocrase-garnet association described below.

Occurrence.

The limestone of the quarries is a light grey, rather coarsely crystalline marble. It has darker bands indicating the bedding planes, and these dip at very low angles to the south. To the north-west the limestone appears to pass downward into a sillimanite-biotite-hornfels containing a sill-like mass of epidiorite; these beds are in contact with a cross-cutting biotite-rich granite. In small exposures near the granite, calc-silicate bands are common in the bedding planes, but in the pure limestone such minerals are confined to the margins of cross-cutting dikes and veins.

Exposed in the eastern quarry is a granitic dike which strikes E.-W. and dips steeply N. As is common with many of the minor intrusions of this area, a band of pegmatite is developed on the hanging wall. The dike has a sheath of calc-silicate minerals, of which garnet and idocrase are the most important species. One narrow cross-cutting dike, besides being enclosed by a sheath of calc-silicates, sends off numerous thin apophyses along the bedding planes, and these pass, within a short distance, into idocrase-garnet veins. Associated with the dikes are smaller veins characterized by a wollastonite-idocrase-garnet assemblage in which the wollastonite forms an outer zone as illustrated in figs. 1, 4, and 7.

These veins vary in composition from a mere whitened limestone to calc-silicate assemblages. Such extremes are present together in the western quarry where a thick, heavily mineralized vein dips steeply N. 36° W. In the immediate neighbourhood of the veins the limestone is whitened in broken streaks which conform to a structural pattern of two planes, one dipping at 40° N. 240° W., and the other steeply N. 105° W. Only in the strike of the first of these planes is there any relationship to the present joint system. In the eastern quarry some veins probably connect with the pegmatitic top of the dike.

The main dike is somewhat boudinaged and the smaller dikes and veins are gently folded and contain minute tension cracks. It can be shown that a late tectonic phase of minor importance affects the area.

Mineralogy.

The chief minerals of the skarn veins are wollastonite, grossular, idocrase, diopside, and tremolite. The properties of each of the last four species vary slightly and therefore the determinations recorded below were made on minerals in juxtaposition. The wollastonite occurs in a white fibrous form often with a radiating structure; cleavage parallel to (100) is evident and twinning parallel to (100) is frequent. Laths showing cleavage traces exhibit a very small extinction angle, showing that the optic axial plane is slightly inclined to the axis of the cleavage zone. This fact is discussed by Peacock (3), who shows that the wollastonite of skarns is triclinic. The refractive indices are α 1·619, γ 1·634, the optical sign is negative, and the specific gravity 2·86.

The garnet is a flesh-coloured variety and occasionally shows striated (211) faces; it is completely isotropic, with a refractive index n 1·753 and a specific gravity of 3·56. These properties indicate an approximate composition of $Gr_{88}And_{12}$.

Idocrase occurs as yellowish-brown striated octagonal prisms with the following optical properties: ω 1·706, $\omega-\epsilon$ 0·006, uniaxial negative sign; pleochroism noticeable in thick section, ϵ faint yellow, ω colourless; zoning frequent; the specific gravity is 3·39.

Small crystals of a greenish diopside show the characteristic cleavages and have a refractive index γ 1·701, $\gamma-\alpha$ 0·29; biaxial positive sign with 2V moderate and $\gamma:c$ = ca. 39°. A green chlorite fills cleavage-cracks in the mineral. The optical properties are comparable with a diopside of the approximate composition $Di_{90}He_{10}$.

Fibres of slightly greenish tremolite have a refractive index γ 1·631, $\gamma-\alpha$ 0·026; biaxial negative sign with 2V large and $\gamma:c$ = ca. 19°.

Brownish pleochroic sphene showing its characteristic form is associated with diopside and idocrase in one of the veins, and it is interesting to note that this mineral is a typical accessory in the granite of the area.

This simple mineralogy is in contrast to that of other calc-silicate localities in the area, where epidote and other minerals enter the suite. These latter occurrences are found at the gradational junction of limestone, and pelitic sediments in proximity to the granite and their formation is influenced by the bedding planes.

Petrology.

The limestone consists of a grey equigranular aggregate of calcite containing disseminated specks of graphite, many of which show hexagonal form. Occurring less abundantly are small flakes of white mica, grains of quartz, and a few scattered grains of epidote. Darker bands contain a greater abundance of graphite and mica with scanty pyrite. The amount of these impurities is variable, ranging, at least, from 10 % in a limestone with many dark bands to over 3 % in the more normal type. On partial analysis a typical grey limestone gave the following composition:

Table 1. Partial analysis of Lough Anure limestone. The insoluble residue obtained by treatment with hydrochloric acid consists in the main of graphite, muscovite, and quartz, together with a much lesser quantity of yellowish pleochroic epidote and a magnesia-mica.

Partial chemical analysis.	%	Calculated modal analysis.	%
CaO	50·56	Calcium carbonate	90·20
MgO	2·99	Magnesium carbonate... ...	6·25
Acid insolubles	3·20		

The period of regional metamorphism and injection which preceded emplacement of the late granite was responsible for recrystallization and formation of graphite from carbonaceous matter. Calcite and silica remained uncombined in this presumably deep-seated environment.

The granite dikes are later than the surrounding modified granodiorite and are petrologically similar to the late alkali-granite. They consist of microcline, albite-oligoclase, quartz, and brown biotite. The smaller dikes are richer in microcline, and accessory calc-silicate minerals such as diopside, garnet, and sphene occur instead of biotite. Granite-pegmatites associated with limestone and containing calc-silicates have been noted and discussed by several writers including Eskola (4), Read (5), Osborne (6, 7), and von Eckermann (8).

Minor cataclasis is shown by granulation and suturing of grains in the main granite and the dike series, and is consistent with the phenomena of minor tension cracks, boudinage, and foliation already noted.

The skarn veins fall into two categories; those with and those without a central magmatic dikelet. The former are confined to the eastern quarry and are probably connected with the pegmatitic top of the main granite dike. Typical examples of each type are described below to illustrate the main features of these veins, which are as follows:

(A) The removal of graphite from the grey limestone in proximity to a quartz vein.

(B) The formation of zones of calc-silicate minerals adjacent to a quartz-felspar vein.

(C) The occurrence of calc-silicates both as an enveloping sheath and as accessory minerals in a plagioclase-microcline dike.

(D) The occurrence of a thick skarn vein without a central magmatic dikelet, but with a much greater development of idocrase and grossular.

A. *The removal of graphite.* -The most conspicuous result of all the veining is the whitening of the grey limestone. This is especially well exhibited by one of the small veins, near which a sharp demarcation exists between grey and whitened limestone; this is shown in fig. 1. The vein is 1·5 mm. in width and consists of quartz containing minute calcite granules with a string of isotropic garnet grains forming a central portion and recrystallized calcite in the fork. Quartz-filled re-entrants which protrude into the limestone on either side contain both diopside and calcite granules. Small xenoblastic grains of diopside are present in both white and grey areas of the limestone. The amount of the mineral is, however, no more than could have resulted from combination of original silica and magnesia, and no appreciable maximum is shown in its concentration.

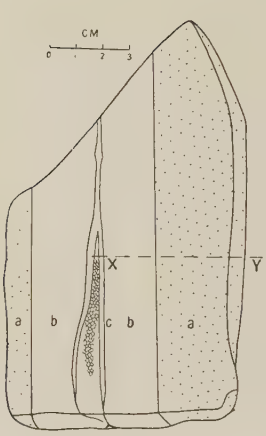

Fig. 1.

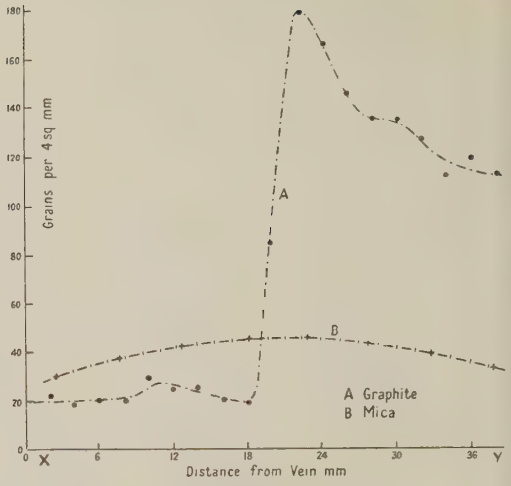

Fig. 2.

Fig. 1. Crystalline limestone with bifurcating quartz vein and showing sharp boundaries of zone free from graphite. *a*, grey graphitic limestone. *b*, white limestone. *c*, quartz vein.

Fig. 2. Count of mineral grains per 4 square mm. across wall-rock. Section XY of fig. 1.

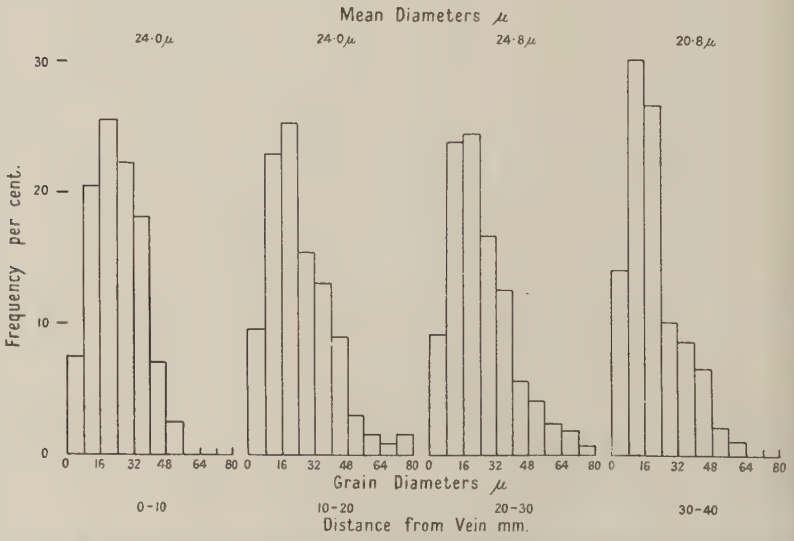

Fig. 3. Histogram showing the frequency per cent. of graphite grain-sizes at intervals across wall-rock of vein shown in fig. 1.

The graphite granules are found to be concentrated at the sharp demarcation line, as can be clearly seen from the graph of fig. 2. Comparison of the size frequencies of the graphite granules (fig. 3) shows that there is an increase in the frequency of the larger sizes immediately beyond the culmination point, with a corresponding increase in mean

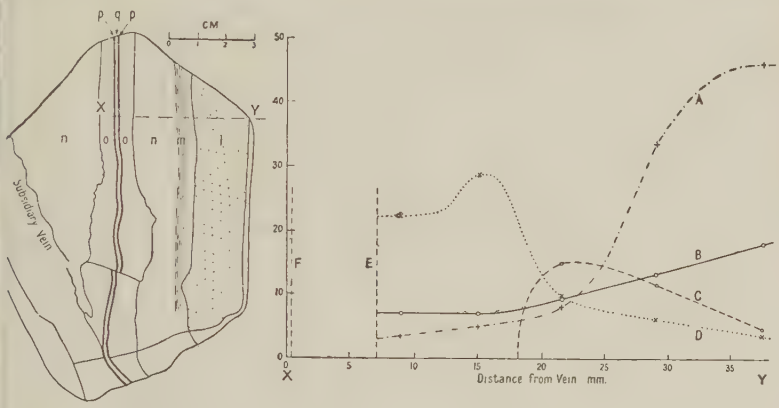

Fig. 4. Fig. 5.

Fig. 4. Crystalline limestone with quartz-felspar vein showing bordering zones of calc-silicates. *l*, grey limestone. *m*, tremolite zone. *n*, diopside zone. *o*, wollastonite zone. *p*, idocrase sheath. *q*, quartz-felspar vein.

Fig. 5. Count of mineral grains per sq. mm. in a section of normal thickness across wall-rock of vein. Section XY of fig. 4.

A, graphite grains. B, quartz and muscovite. C, tremolite. D, diopside. E, limit of wollastonite. F, idocrase sheath to vein.

diameter. This latter factor is seen to have higher values within the affected zone than in the outer limestone. These facts indicate that the maximum shown by curve A, fig. 2, would be accentuated if it could be corrected to represent more nearly the true volume of graphite, and it is thus likely that the amount of graphite removed is approximately the same as that in excess of the normal concentration at the culmination point. Little, if any, graphite has been removed from or added to the system. The mica flakes, which are of similar size and shape to the graphite particles, are only slightly concentrated, and it would, therefore, appear that a purely mechanical explanation of the movement of the graphite is not feasible. The average size of the calcite granules is constant and there is no evidence of recrystallization at any appreciable distance from the vein, though this has occurred between the bifurcation shown in fig. 1.

B. *The presence of calc-silicate zones.*—A second case of skarn formation is that shown in fig. 4, in which a cross-cutting vein, 2 mm. in width and consisting of orthoclase, plagioclase, and quartz is bordered by crustified idocrase which has a replacement relationship towards an outer zone of wollastonite (fig. 6c).

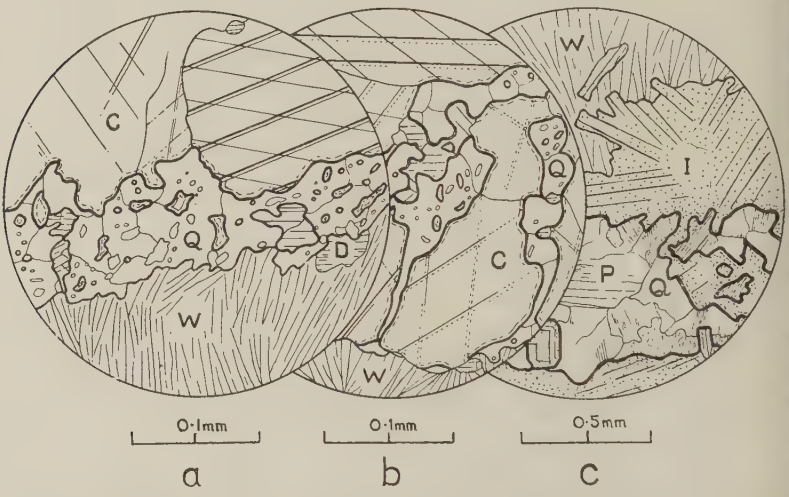

Fig. 6. Central portions of skarn vein, fig. 4.

(*a*) Calcite-wollastonite boundary with intervening quartz selvedge containing calcite granules.

(*b*) Penetration of quartz along grain boundaries of calcite.

(*c*) Central portion of vein showing idocrase replacing wollastonite. Well-formed crystals penetrate into the plagioclase-quartz dikelet.

C, calcite. D, diopside. I, idocrase. P, plagioclase. Q, quartz. W, wollastonite.

The wollastonite forms a band on either side, averaging 5 mm. in width and with fibres approximately perpendicular to the vein. At the sharp junction between this mineral and the calcite there is a thin selvedge of quartz containing granules of calcite and some wollastonite (fig. 6a); this is especially well developed where there are inter-granular projections into the limestone (fig. 6b), but here diopside is formed instead of wollastonite. There is no similarity between the opposite wollastonite-calcite boundaries, and it is reasonable to assume that the wollastonite is a result of a reaction between the limestone and silica introduced from the vein. The quartz containing the calcite granules is thus the result of 'freezing' the well-known reaction $CaCO_5+SiO_2 \rightleftharpoons CaSiO_5+CO_2$. With assumptions as to the pressure this will determine an isotherm in the heat exchange between the vein and the wall rock.

As in the first case described above there is a whitened zone quite sharply demarcated from the grey limestone, and the distance of this demarcation from the quartz selvedge is approximately the same in both cases (23 mm.). The whitened area of limestone contains two mineral zones, an inner one containing granular diopside and an outer containing fibrous tremolite. This latter zone is shown as a narrow greenish band in the specimen illustrated in fig. 4 and is approximately 22 mm. from the centre of the vein. The diopside persists within the band of wollastonite, but exhibits a sharp decrease in concentration at a distance of 17 mm. from the vein (fig. 5). Beyond this point the concentration of tremolite rises rapidly to a maximum and then falls more gradually outward from the vein. In the very outermost zone examined, small fibrous aggregates of a moderately birefringent mineral occur, often as a reaction rim to grains of a greenish mineral which is probably a chlorite.

The quartz shows a decrease *pari passu* with silicate formation, and quartz grains in outer zones commonly contain acicular tremolite. The sequence of mineral zones is thus idocrase and wollastonite, diopside, tremolite, and magnesia-poor limestone containing free quartz and graphite.

C. *Occurrence of accessory calc-silicates.*—Some of the thicker felspathic dikelets also develop sheaths of wollastonite, diopside, and bleached limestone, and in this type it is the magmatic portion which is of interest. One of the dikes, essentially composed of microcline, orthoclase, a lesser amount of plagioclase, and a little quartz, contains abundant idiomorphic diopside, brownish sphene, and small needles of apatite. Towards the contact with the bordering skarn, the dike contains fragments of calcite fringed with calc-silicates; idocrase becomes a common constituent and may be accompanied by a little zoisite. Considerable addition of lime has evidently been made to the intrusion both by incorporation of calcite and by reciprocal exchange of lime for silica.

Outward from the centre of the dikelet the felspars become increasingly turbid until they are nearly opaque at the contact; this alteration is due to the presence of minute moderately birefringent flakes, possibly produced at the time of silicate formation by a process akin to kaolinization.

D. *The thick skarn veins.*—In the principal skarn vein of the quarry, mineralization is intense (fig. 7). As in the above types, there is an outer zone of bleached limestone with diopside, but the wollastonite zone is

more variable in thickness, and at the junction with the limestone the calcite is often recrystallized in relatively large grains.

In this case no quartz selvedge is present at the wollastonite boundary, where the marginal re-entrants and relict areas of calcite leave little doubt that the silicate has replaced calcite. Idocrase and garnet form a

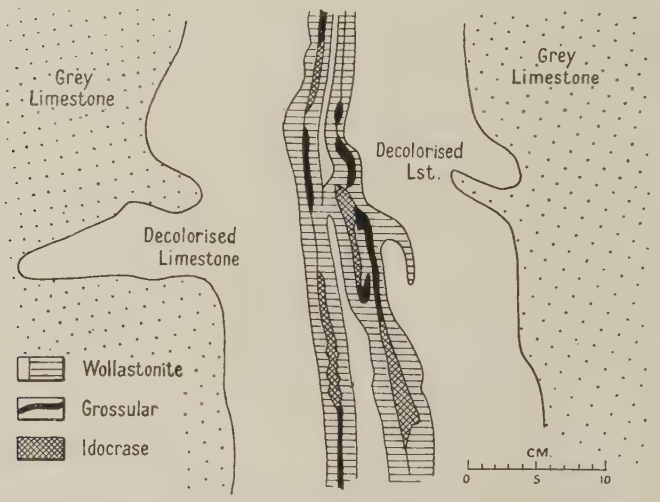

Fig. 7. Sketch of main calc-silicate skarn vein. Western quarry, Lough Anure. Vertical section.

central portion with relict areas of calcite and wollastonite, and here there is no plagioclase-quartz veinlet. The zoned idocrase contains residual fibres of wollastonite, diopside granules, and relict areas of calcite. Small areas of quartz are present, bordered by euhedral idocrase; the former mineral seems to have been released by the replacement of wollastonite by the aluminous calc-silicates.

The relationship in time of the garnet and idocrase is more difficult to assess. Contained within the garnet are relict areas of idocrase characterized by optical continuity and the identity of zonal bands; less commonly relics of garnet are present in the idocrase. Bearing in mind the similarity in structure between the two minerals, their intimate relationships are interpreted as evidence of simultaneous formation (fig. 7).

A feature of this particular skarn vein is the concentration of diopside granules in a line parallel and very near to the wollastonite-calcite boundary. The intervening calcite contains many less granules than the outer limestone, and this particular concentration is interpreted as a

sweeping outwards of impurities during recrystallization of the calcite adjacent to the vein. This mechanical effect is thus seen to be of small importance even where mineralization has been most intense.

Discussion.

The removal of graphite.– The most striking effect of the action of the introduced material is the removal of carbon from the limestone in its immediate vicinity with a resultant piling-up of graphite beyond a knife-sharp demarcation line. This decolorizing effect is well known, though the resulting concentration near the vein may not be so widely recognized.

A hypothesis of simple distillation cannot be entertained, for the carbonaceous material was almost certainly graphitic at the time of the intrusion of the granite dikes. The fact that the mica flakes are relatively unmoved lends support to the hypothesis of A. N. Winchell (9) that the removal of graphite is mainly the result of a chemical process in which two interdependent reactions are possible: $C + 2H_2O \rightleftharpoons CO_2 + 2H_2$, and $C + CO_2 \rightleftharpoons 2CO$. The hydroxyl ion is necessarily present in both idocrase and tremolite and the presence of carbon dioxide is certain, for it was released in the formation of wollastonite from limestone. It is remarkable, however, that even where the silicate zone is negligible the limestone is still bleached and the graphite concentrated in an outer zone. Whilst it is possible that the carbon dioxide from silicated areas was swept along the veinlet, water vapour must be considered as the important factor in these reactions. Both reactions are displaced to the right by a rise in temperature and to the left by an increase in pressure. Under conditions of constant volume a temperature gradient would allow removal of carbon near the vein with deposition at a certain distance. Such conditions would be expected to produce a variation in grain-size frequency, especially an increase in the zone of deposition. In such a system with two possible gas phases, equilibrium can obtain over a wide range of temperatures, but, although the reactions under discussion are initiated at temperatures below 500° C., that involving steam is of negligible *rate* below 550° C., and that involving carbon dioxide is negligible below 600° C.; according to Taylor and Neville (10) the presence of calcium carbonate has only a slight catalytic effect. Even at temperatures 100° C. higher the reactions are slow, and Winchell (9) considers that 700° C. is a lower limit of appreciable transport of carbon. Higher pressures raise the temperature required to maintain a particular state of equilibrium, but the velocity of the reaction is probably not affected.

The grain-size frequency histograms of fig. 3 show features in accord with such a means of transport, especially as the suggested mechanism involves a surface reaction. The histogram on the right of fig. 3 represents the original size frequency of the graphite grains and shows an acute maximum in the small grain-sizes. The smaller the grain the greater is the surface area relative to the volume and, as the efficiency of solution or reaction is a function of area, the smaller the grain the more rapidly will it be removed. Thus the continued removal of graphite near the vein led to a relative decrease in the frequency of the smaller grain-sizes with a resultant increase in the mean diameter. Deposition of some part of the graphite on existing grains led to an increase in the frequency of the larger grain-sizes at the graphite culmination.

The skarn zones.—The formation of wollastonite, diopside, and tremolite as zones is very well demonstrated by the data expressed by fig. 5. It is admitted that a count of mineral grains cannot represent true concentrations by weight without a detailed knowledge of size frequencies; thus, for instance, the peak at 15 mm. in the diopside curve D is due to a decrease in grain-size. Nevertheless, the antipathy of this curve to that of tremolite and the curves of both these silicates to that of free quartz is clearly shown, demonstrating the separation of the mineral assemblages. This zoning of the silicates is coincident with a falling temperature gradient at a constant pressure, a factor which was clearly important in their formation. It has long been realized that, at a given pressure, metamorphism of magnesian limestones with excess silica proceeds in a regular sequence of steps with increasing temperature—Eskola (4) and Bowen (11). In the example described, a tremolite-diopside assemblage is first formed, then diopside, and finally a wollastonite-diopside assemblage separated by an idocrase sheath from a vein containing felspar.

It is possible to formulate a number of equations for the formation of tremolite and diopside, for these minerals may arise from talc as a result of a chain of reactions or by direct reaction between dolomite and quartz. This may depend on the rapidity of establishment of a particular temperature of transformation. The following equations are suggested by Bowen (11) for the production of (*a*) tremolite from siliceous dolomite and (*b*) diopside from tremolite:

Low temperature. High temperature.

(*a*) $5CaMg(CO_3)_2 + 8SiO_2 + H_2O = (OH)_2Ca_2Mg_5(Si_4O_{11})_2 + 3CaCO_3 + 7CO_2$.

(*b*) $(OH)_2Ca_2Mg_5(Si_4O_{11})_2 + 3CaCO_3 + 2SiO_2 = 5CaMgSi_2O_6 + 3CO_2 + H_2O$.

The second reaction takes place at a higher temperature than the first.

Some of the diopside granules certainly exhibit a fibrous structure in the outer limits of the zone, which may be a residual feature, but it seems possible that the isotherms determining these reactions were rapidly established allowing formation of both silicates directly from the dolomitic portion of the limestone. Then, presumably, they gradually moved outward a distance equal to the width of the wollastonite zone, for we can assume that the quartz selvedge containing calcite, quartz, and wollastonite represents a definite and constant temperature.

Near the vein illustrated by fig. 4 the diopside constitutes approximately 8 % of the limestone and has evidently utilized the detrital quartz and the magnesia originally present in the form of 6 % magnesium carbonate (table 1). The quartz content in the unaltered limestone near the vein does not exceed 2 %, which thus implies that there was an addition of silica as well as the utilization of the original quartz. These remarks may also apply in the case of tremolite. Such a dual source of silica in skarns has been noted by Lindgren (12), although more generally the original quartz reacts less readily than the already ionized silica introduced from the magma. This introduction can be demonstrated clearly in microsections, for intergranular stringers of quartz bordered by diopside ramify far in advance of the wollastonite boundary. The silica may have been introduced as a solute in super-critical steam, this medium also removing graphite into an outer zone by the reactions discussed above.

The concentration of introduced silica should fall with increasing distance from the vein, for diffusion into the wall-rock depends on the temperature and pressure gradients which fall away from the intrusion. A zoned order of minerals may arise due to the resulting variation in the proportion of silica to magnesia, and it is significant that the minerals tremolite, diopside, and wollastonite are in order of decreasing dedolomitization. The formation of calc-silicate zones associated with a granitic apophysis at Port Shepstone, Natal, is attributed by Hatch and Rastall (13) to a diffusion mechanism with a fall in silica concentration away from the intrusion. Thus several interdependent factors, the temperature, pressure, and silica concentration gradients, are possibly concerned in the genesis of the mineral zones.

A volume for volume replacement of wollastonite for calcite and of idocrase and garnet for wollastonite is assumed. If the compositions are calculated from the optical properties, the comparison of the weights of ions in equal volumes of calc-silicate minerals and magnesia-poor limestone indicates that the calcium ion is not greatly involved in the substitutions. Some small exchange takes place during wollastonite

formation, but not in the replacement of wollastonite by idocrase and grossular, in which case it is the amount of silica per unit volume which decreases as a result of the substitution. This may account for the interstitial quartz with optical continuity which is associated with the grossular and idocrase. There was evidently a primary influx of silica which was in small part released in the form of quartz during the addition of alumina, magnesia, and iron to form grossular and idocrase in the larger veins.

The nature of the wollastonite formation is apparent from the quartz selvedge containing calcite and wollastonite granules. In this simple reaction of silica with calcium carbonate the silica must have been continuously supplied from the intrusion and was probably transported through the enveloping skarn by super-critical steam, as suggested by the experiments of Gillingham (14), in which wollastonite was formed by reaction of steam-borne silica with Iceland-spar. The silica showed different rates of transfer to different 'collectors', indicating that a chemical potential is a possible factor in such a mechanism.

Fig. 4 shows without further discussion that the supply of silica is out of all proportion to the width of the intrusive. The quartz-felspar dikelet must have been continuously replenished, silica being rapidly absorbed by the limestone. In the early stages of the intrusion the material may have been more siliceous and, significantly, vein terminations are quartz-rich and are without appreciable skarn. When felspathic components entered the dikelet idocrase was formed by reaction with the early formed wollastonite. The small quartz-felspathic veins are almost certainly connected to the pegmatitic top of the main granite dike, and it is possible that the highly siliceous fluid originated from this pegmatitic phase. The vapour pressure created by the separation of such a phase may explain the degree of penetration of silica into the limestone wall-rock.

The main skarn vein may be the upward extension of a thinning pegmatite, for, as noted above, small granitic apophyses are seen to pass into skarn veins at a distance from the main intrusion.

The temperature of formation.—The well-known reaction expressing the formation of wollastonite can only be univariant in a closed system. Certainly the vapour pressure of the carbon dioxide would be reduced by dissipation in such metasomatic processes, with the result that the temperature of formation may be lowered to an unknown extent. This aspect is fully discussed by Eskola (4) and Bowen (11). The fact that bleaching occurs along structural planes in the western quarry of Lough

Anure and is common along bedding planes in many other granite-limestone areas indicates that the system may be relatively open. The association of calcite, quartz, and wollastonite reveals that there was a maximum temperature above which the quartz selvedge was never raised; namely, the temperature at which the reaction $CaCO_3 + SiO_2 \rightleftharpoons CaSiO_3 + CO_2$ is in equilibrium at a certain pressure.

The temperature relations of the system CaO–SiO_2–CO_2 have been investigated in great detail by Kröger and Illner (15 A) at normal pressures. With silica in excess of calcium carbonate, the metasilicate reaction becomes stabilized at about 550° C., but commences at much lower temperatures. In the experiments of Gillingham (14) wollastonite was formed at temperatures as low as 405° C. at a pressure of 248 atmospheres, but no attainment of equilibrium is claimed. Whilst it is possible for wollastonite to form at quite low temperatures, it would seem that the Goldschmidt pressure-temperature diagram as reproduced by Bowen (11) is a probable approximation and almost certainly an upper limit for reaction temperatures under conditions of equilibrium. At a pressure of one atmosphere an equilibrium reaction temperature not far below 500° C. is postulated, at an assumed pressure of 800 atmospheres (where the gradient of this P.T. curve becomes small and nearly parallel to the pressure abscissa) this temperature is near 750° C. and is the upper limit of the temperature of skarn formation. In the relatively open system of Lough Anure the temperature will be considerably lower, depending on the degree of escape of the carbon dioxide.

The reaction is, however, complicated by the presence of foreign substances (15 B). Whilst steam does not influence the reaction, halides increase the velocity and the presence of fluorine raises the temperature of stabilization. As idocrase accompanies wollastonite at Lough Anure fluorine was possibly present during the formation of the latter mineral.

As discussed above, 500° C. may be the minimum temperature for the transport of carbon, but even at temperatures 100° C. higher the reaction is slow and time is not unlimited when such minor intrusions are considered. Although it is not possible to be precise with regard to the actual temperature it was certainly well below 750° C., and on the present hypothesis for carbon removal some temperature above 550° C. might be expected. The great width of the skarn envelope compared with that of the dikelet suggests that the temperature gradient from the vein cannot have been steep, and it is possible that the temperature of the whole sedimentary mass may have been raised by the approach of the later granite and intrusion of the larger dikes.

Summary.—A series of calc-silicate skarn veins is described; these occur in a limestone mass surrounded by granite in the Dalradian of western Donegal.

The skarn which borders these veins exhibits a zonal arrangement of the constituent minerals, idocrase and garnet, wollastonite, diopside and tremolite, which are enveloped by a zone of decolorized limestone. A central quartz-felspar dikelet is present in some cases.

The processes envisaged are the removal of graphite to an outer zone by means of a reversible reaction involving carbon dioxide or water; the addition of silica to yield wollastonite in an inner zone and diopside and tremolite in outer cooler zones, followed by an influx chiefly of alumina to produce idocrase and grossular by replacement of the wollastonite.

The sequence of zones is that of the established order of silicate formation with increasing temperature in a dolomite with excess quartz. The presence of wollastonite and calcite in equilibrium with quartz is taken to indicate a temperature lower than 750° C., and a temperature higher than 550° C. is probable for reactions involving the removal of graphite.

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References.

1. Hull (E.) and others, North-west and central Donegal. Mem. Geol. Surv. Ireland (Explanation of sheets 3–5, &c.), 1891.
2. Scott (R. H.), On the mineral localities of Donegal, as ascertained by Sir Charles Giesecke... Journ. Roy. Dublin Soc., 1863, vol. 4, pp. 114–125.
3. Peacock, M. A., On wollastonite and parawollastonite. Amer. Journ. Sci., 1935, ser. 5, vol. 30, pp. 495–529. [M.A. **6**–260.]
4. Eskola (P.), On contact phenomena between gneiss and limestone in western Massachusetts. Journ. Geol. Chicago, 1922, vol. 30, pp. 265–294. [M.A. **2**–437.]
5. Read (H. H.), A diopside-bearing pegmatite near Ellon in Aberdeenshire. Trans. Edinburgh Geol. Soc., 1925, vol. 11, pp. 353–356. [M.A. **3**–37.]
6. Osborne (C. D.), The metamorphosed limestones and associated contaminated igneous rocks of the Carlingford district Co. Louth. Geol. Mag., 1932, vol. 69, pp. 209–233.
7. —— The contact metamorphism and related phenomena in the neighbourhood of Marulan, New South Wales. Part I. The quartz-monzonite–limestone contact. Geol. Mag., 1931, vol. 68, pp. 239–314. [M.A. **4**–513.]
8. Eckermann (H. von), Rocks and contact minerals of the Mansjö Mountain. Geol. För. Förh. Stockholm, 1922, vol. 44, pp. 203–410. [M.A. **1**–396.]
9. Winchell (A. N.), Petrographic studies of limestone alterations at Bingham. Trans. Amer. Inst. Min. Met. Eng., 1924, vol. 70, pp. 884–903.

10. Taylor (H. S.) and Neville (A.), Catalysis in the interaction of carbon with steam and with carbon dioxide. Journ. Amer. Chem. Soc., 1921, vol. 43, pp. 2055–2071.

11. Bowen (N. L.), Progressive metamorphism of siliceous limestone and dolomite. Journ. Geol. Chicago, 1940, vol. 48, pp. 225–274. [M.A. **8**–243.]

12. Lindgren (W.), Contact metamorphism at Bingham, Utah. Bull. Geol. Soc. Amer., 1924, vol. 35, pp. 507–534.

13. Hatch (F. H.) and Rastall (R. H.), Physical chemical geology. London, 1927, p. 147.

14. Gillingham (T. E.), The solubility and transfer of silica and other non-volatiles in steam. Econ. Geol., 1948, vol. 43, pp. 241–272.

15a. Kröger (C.) and Illner (K. W.), Über die Systeme Alkalioxyd–CaO–Al_2O_3–SiO_2–CO_2. VI. Zeits. Anorg. Chem., 1936, vol. 229, pp. 197–224 (p. 204).

15 b. —— —— VII. Ibid., 1939, vol. 240, pp. 273–283.

Aluminium replacing silicon in some silicate lattices.

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THE purpose of this account is to review, from the literature, figures for the replacement of silicon by aluminium in biotites, calciferous amphiboles, and clinopyroxenes. Atomic ratios to be quoted have been calculated on a basis of 24(O,OH,F) in biotites, hornblendes, and pyroxenes alike. This facilitates comparison and the higher factor magnifies differences. It may be emphasized, to avoid possible confusion, that in this discussion it is the amount of silicon replaced by aluminium that will be under review. The ratio of tetrahedrally co-ordinated Al to octahedrally co-ordinated Al will not be considered, although for the sake of completeness, figures for Al in *Y* groups will be furnished to show total Al values. Machatschki's group notation is employed. Comparison between biotites, hornblendes, and clinopyroxenes, for present purposes, may best be made between minerals that crystallized under the same pressure-temperature conditions, to reduce variables. Few analyses of specimens of these three minerals, that have crystallized together in the same rock, are available however. One such paragenesis is quoted below. This association occurs as gneiss-like inclusions in calcite, taken from the Tiree marble.[1]

		Pyroxene.	Hornblende.	Biotite.
Z ...	Si	7·468	6·14	5·56
	Al	0·532	1·86	2·44
Y ...	Al	0·284	0·89	0·52

Despite the lack of information regarding such associations from the same rock, comparison between biotite, hornblende, and clinopyroxene may be made when those minerals have crystallized during the orthomagmatic stage of plutonic igneous activity. Their conditions of formation will then have been approximately similar. The following average values for igneous biotite have been taken from Nockolds.[2]

The atomic ratios of silicon and aluminium in the *Z* group of magmatic hornblendes varies largely within the limits Si 6·40, Al 1·60 and Si 5·60,

[1] A. F. Hallimond, Min. Mag., 1947, vol. 28, p. 230.

[2] S. R. Nockolds, Amer. Journ. Sci., 1947, vol. 245, p. 401. [M.A. 10–271.]

Average values for biotites from calc-alkaline plutonic rocks.

Associated mineral ...		Topaz.	Muscovite.	Biotite alone.	Hornblende.
Z ...	Si	5·89	5·30	5·49	5·53
	Al	2·11	2·70	2·51	2·47
Y ...	Al	1·42	0·78	0·38	0·15

Average values for biotites from alkaline plutonic rocks.

Associated mineral ...		Biotite alone.	Alkali-amphibole.	Aegirine.
Z ...	Si	5·48	5·63	5·52
	Al	2·52	2·37	2·48
Y ...	... ...	0·44	0·05	—

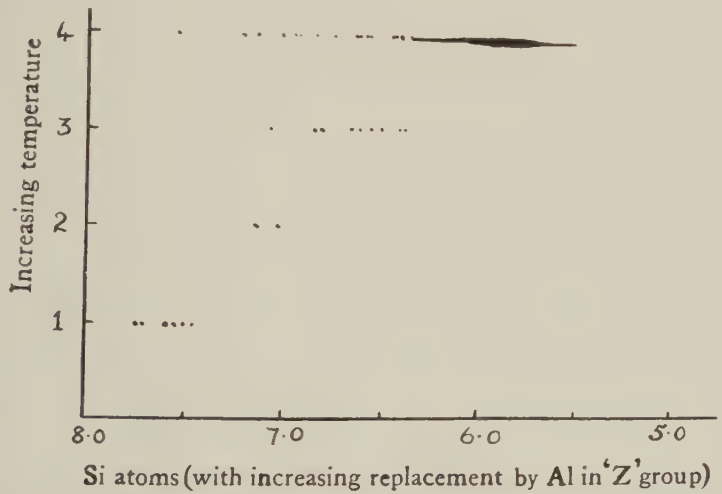

FIG. 1. Plot of hornblende analyses from: 1, green-schist metamorphic facies; 2, albite-epidote-amphibolite facies; 3, amphibolite facies; 4, igneous rocks.

Al 2·40. There is, however, a decline in the number of magmatic hornblende analyses showing values for aluminium substitution in the *Z* group exceeding the ratio Si 6·00, Al 2·00. These general relations are exemplified by fig. 1, in which the atomic ratios of silicon in these amphiboles are plotted on a horizontal line. Isolated dots on this line indicate individual analyses. Where the dots representing the latter become too closely spaced to permit differentiation they are represented as a solid line, thickest where the analyses are most abundant. The data have largely been selected from 196 igneous and metamorphic calciferous amphiboles quoted by Hallimond.[1]

[1] A. F. Hallimond, Amer. Min., 1943, vol. 28, p. 65. [M.A. 9–270.]

The magmatic pyroxenes have been recently discussed by Niggli.[1] Representative values for plutonic clinopyroxenes are quoted below.

		I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Z	Si	7·56	7·588	7·200	7·288	7·332	7·140	7·468	7·344	7·448	7·340
	Al	0·44	0·412	0·800	0·712	0·668	0·860	0·532	0·608	0·552	0·660
Y	Al	0·07	0·160	0·048	0·108	0·240	0·172	0·580	—	0·332	0·116

I. S. R. Nockolds and R. L. Mitchell, Trans. Roy. Soc. Edinburgh, 1948, vol. 61, p. 560. [M.A. **10**–424.]

II–III. S. R. Nockolds, Geol. Mag., 1938, vol. 75, p. 469. [M.A. **7**–304.]

IV–X. L. R. Wager and W. A. Deer, Medd. Grønland, 1939, vol. 105, no. 4. [M.A. **8**–27.]

I is taken from peridotite, the rest from gabbroic rocks.

The biotites, hornblendes, and pyroxenes cited have all been selected from plutonic rocks. The composition of a mineral as crystallization proceeds and temperature declines may reflect one or both of two factors, the stability requirements of the lattice and the composition of the magma. Rapidly crystallizing minerals may form metastable phases, however, in which case the control exerted by lattice requirements may be wholly eliminated. Ratios for minerals taken from effusive rocks have therefore been omitted.

It will be seen above that the degree to which aluminium replaces silicon in the biotites, calciferous amphiboles, and clinopyroxenes of igneous plutonic rocks is characteristic for each mineral group. Further, this replacement value is greatest in the biotites, of intermediate magnitude in the amphiboles, and least in the pyroxenes.

Comparisons may now be made between the members of one mineral group to investigate the manner in which the degree of Si–Al substitution varies with different physical conditions of crystallization. For such a purpose the calciferous amphiboles are admirably suited, possessing a wide field of chemical stability and persisting as stable minerals from the green-schist facies to the amphibolite facies, the latter being widespread in regional metamorphic terrains. Moreover, passage between the two facies is a normal sequence in progressive metamorphism and appears to be dominantly controlled by rising temperatures, thus simplifying the discussion in terms of operative physical variables. The effect of rising temperatures upon Si–Al substitution in the calciferous amphiboles may be seen from the following atomic ratios for calciferous amphiboles taken from the green-schist facies, epidote-albite-amphibolite facies, and the amphibolite facies. These hornblendes comprise the vast majority of the rock-forming amphibole varieties. Those amphiboles

[1] P. Niggli, Schweiz. Min. Petr. Mitt., 1943, vol. 23, p. 538.

omitted from discussion, cummingtonite, grunerite, and the glaucophanes, are unusual species, often occurring in parageneses of doubtful significance.

Amphiboles from the green-schist metamorphic facies.

		I.	II.	III.	IV.	V.	VI.
Z	Si	... 7·743	7·734	7·591	7·610	7·537	7·474
	Al	... 0·257	0·244	0·409	0·406	0·463	0·526
Y	Al	... 0·193	0·022	0·189	0·053	0·206	0·127

I–II. From hornblende-epidote-albite-schist, South Devon. C. E. Tilley, Geol. Mag., 1938, vol. 75, p. 497. [M.A. **7**–446.]

III. From hornblende-talc-chlorite-schist, South Devon. C. E. Tilley, ibid.

IV. From chlorite-epidote-albite-amphibolite, Argyll. J. D. H. Wiseman, Quart. Journ. Geol. Soc., London, 1934, vol. 90, p. 354. [M.A. **6**–224.]

V. From albite-stilpnomelane-actinolite-schist. C. O. Hutton, Mem. Geol. Surv. New Zealand, 1940, no. 5. [M.A. **8**–19.]

VI. From albite-epidote-actinolite-calcite-schist. C. O. Hutton, ibid.

Amphiboles from the epidote-albite-amphibolite facies.

		I.	II.
Z	Si	... 7·160	7·062
	Al	... 0·840	0·938
Y	Al	... 0·562	0·547

I. From garnet-biotite-epidote-albite-amphibolite. J. D. H. Wiseman, ibid.

II. From biotite-epidote-albite-amphibolite. J. D. H. Wiseman, ibid.

Amphiboles from the amphibolite facies.

		I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Z	Si ...	6·69	6·63	6·40	7·10	6·41	6·82	6·59	6·52
	Al ...	1·01	1·37	1·60	0·90	1·59	1·18	1·41	1·48
Y	Al ...	—	0·97	0·57	0·62	0·48	1·30	0·86	0·11

I. L. Duparc and F. Pearce, Bull. Soc. Franç. Min., 1908, vol. 31, p. 118.

II. S. Tsuboi, Japanese Journ. Geol. Geogr., 1936, vol. 13, p. 333. [M.A. **7**–30.]

III. A. Marchet, Tschermak's Min. Petr. Mitt., 1925, vol. 38, p. 500. [M.A. **3**–82.]

IV, and V. T. Du Rietz, Sveriges Geol. Undersök., 1938, Ser. C, no. 416, p. 70. [M.A. **8**–235.]

VI. L. Hezner, Tschermak's Min. Petr. Mitt., 1903, vol. 22, p. 562.

VII. P. Eskola, Vid.-Selsk. Skr., I. Math.-nat. Kl., 1921, vol. 1, no. 8. [M.A. **2**–313.]

VIII. A. W. Groves, Quart. Journ. Geol. Soc. London, 1935, vol. 91, p. 158.

The first seven of these examples were taken from amphibolites. VIII is from charnockite in which the amphiboles represent adjustments to the amphibolite facies. VI and VII are derived from altered eclogites.

The figures given indicate that with rising metamorphic temperatures silicon in the Z group of the calciferous amphibole structure is progressively replaced by aluminium. In this connexion it is interesting

that among the examples taken from the green-schist facies, numbers V and VI, which for the hornblendes cited from that facies are richest in tetrahedrally co-ordinated aluminium, were taken from rocks in Hutton's 'chlorite 4 sub-zone' near the top of the facies. Amongst those specimens cited from the amphibolite facies, number IV, with the smallest amount of aluminium in substitution for silicon, is a pale-coloured variety in contact and intimate association with mica-schist and occurring with appreciable amounts of chlorite. It appears to represent a lower metamorphic grade than is shown by the other hornblendes in the amphibolite facies table. The amount of tetrahedrally co-ordinated aluminium in the metamorphic calciferous amphiboles appears then to be a direct function of the temperature at which crystallization took place at equilibrium.

Hornblendes with greater values for Al in Si–Al substitution, than shown by those cited, have been recorded from metamorphic rocks in the amphibolite facies. Two such are given below:

			I.	II.
Z ...	Si	...	6·19	6·13
	Al	...	1·81	1·87
Y ...	Al	...	0·52	1·07

I was taken from a garnet-amphibolite, Glenelg[1] and II from a kyanite-amphibolite, Glenelg.[2] Such highly aluminous hornblendes customarily belong to parageneses of doubtful interpretation in which the chemistry of the parent-rock appears to have considerably influenced the nature of the hornblende. Both examples cited are of eclogitic parentage, deriving from omphacite.

Comparison between the two groups of hornblendes, the igneous and metamorphic, may now be made. Their relations are shown in fig. 1. Of 118 calciferous amphiboles cited by Hallimond[3] showing Si–Al ratios in the *Z* group between the limits Si 8·00, Al 0·00 and Si 6·40, Al 1·60, only 33 were taken from igneous rocks. Of these only 13 (chiefly from diorites) may perhaps be accepted as stable under orthomagmatic conditions, the other 20 having either been modified under sub-magmatic conditions or else occurring in lava types in which case they may be in disequilibrium, as discussed. For hornblendes with values for aluminium substitution higher than Si 6·40, Al 1·60 the proportion of igneous to metamorphic hornblende increases rapidly, until the latter are excluded

[1] A. R. Alderman, Quart. Journ. Geol. Soc. London, 1936, vol. 92, p. 519.
[2] C. E. Tilley, Min. Mag., 1937, vol. 24, p. 565.
[3] A. F. Hallimond, Amer. Min., 1943, vol. 28, p. 65. [M.A. 9–270.]

for Si values less than 5·90. Passage from metamorphic to magmatic conditions appears to take place in the calciferous amphibole series with increase in aluminium replacing silicon.

A further relevant point is raised by the following data, taken from Nockolds and Mitchell,[1] and Deer.[2]

Average values for hornblendes from some Caledonian plutonic rocks.

		I.	II.	III.
Z ...	Si ...	6·31	6·79	7·12
	Al ...	1·69	1·21	0·88
Y ...	Al ...	0·22	0·11	0·15

I. Average values of 5 early hornblendes in appinitic types.

II. Average values of 6 primary hornblendes in diorites and trondjhemites.

III. Average values of 4 late crystals from various chemical environments.

Of group III Nockolds and Mitchell suggest that all hornblendes in that group may be the products of late solutions altering pre-existing pyroxenes and primary amphiboles. The figures demonstrate a decrease in the amount of aluminium substituting silicon with declining temperature of formation. Within the calciferous amphiboles the proportion of tetrahedral aluminium therefore apparently increases from the lowest metamorphic grade to the field of magmatic activity. The amount of tetrahedral aluminium within this group appears to reflect the temperature of formation of different species and may perhaps be used with due care as a geological thermometer and aid in discussion of facies within the range of normal progressive metamorphism. The increasing entry of alumina into calciferous hornblende with increasing metamorphic grade is well known, and is exemplified by the passage: pale amphibole—blue-green hornblende—common green hornblende—brown hornblende (magmatic). To the best of the writer's knowledge, however, no one has yet drawn attention specifically to the function of tetrahedrally co-ordinated aluminium atoms.

In discussion, a point has occasionally been made in recent years of the fact that passage from one member of Bowen's discontinuous reaction series to another member of the series takes place by fundamental changes in the atomic configurations of the minerals concerned. Progressing from low to higher temperature members of the series, sheet

[1] S. R. Nockolds and R. L. Mitchell, Trans. Roy. Soc. Edinburgh, 1948, vol. 61, p. 560. [M.A. **10**–424.]

[2] W. A. Deer, Min. Mag., 1938, vol. 25, p. 56.

lattices (e.g. biotite) are succeeded in turn by double-chain structures (amphiboles), single-chain arrangements (pyroxenes), and isolated tetrahedral units (olivines). In a reaction pair, transformation to the higher-temperature member is effected by the severance of certain bonds binding the tetrahedral units together. By such bond breakages infinite tetrahedral sheets (e.g. micas) may eventually be reduced to individual tetrahedra. Since reactions in the direction mica → olivine result with rising temperature, the accompanying successive bond breaks may be roughly conceived as taking place largely in response to increased thermal agitation of the lattice. Biotites, hornblendes, and pyroxenes may nevertheless crystallize together in stable equilibrium. Since the figures quoted for Al substitution are greatest in the most complex structure (biotite) and least in the pyroxenes, it may appear that tetrahedrally co-ordinated Al stabilizes the former under physical conditions promoting crystallization of simpler lattice types. The charge ratio between Al and Si in silicate lattices is 3:4. Replacement of Si by Al therefore leaves the oxygens of the tetrahedral units concerned electrostatically unsatisfied. By Pauling's rules, those oxygens tend to enter into bonds with cations external to the tetrahedra. Buerger[1] thus suggests on these grounds that replacement of Si by Al helps to control the stability of a mineral and its position in the reaction series. On such a basis it might also similarly be argued from data cited that Al plays a corresponding stabilizing role in the higher-temperature hornblendes.

However, replacement of Si by Al instead of strengthening the lattice might actually weaken it by reducing the bond strengths within tetrahedra whilst strengthening bonds to cations outside the tetrahedral units. This might favour breakage of Al–O bonds and simplification of the tetrahedral pattern.

Also low values for Si–Al substitution in the clinopyroxenes may be explained in the following manner. In silicate lattices electrostatic balance must be re-established after such exchanges have taken place. This may be achieved with replacement of cations by others of similar radius but higher charge, by 'building-in' of additional cations, or by substitution of O by OH. In pyroxenes only the first case obtains. This necessitates exchange of divalent cations for tervalent cations of similar size. These are rare, and therefore Si–Al substitution values are generally small in pyroxenes. In the biotites, however, the Mg positions seem narrow and can accommodate smaller tervalent ions like Fe^{3+}. Also

[1] M. J. Buerger, The rôle of temperature in mineralogy. Amer. Min., 1948, vol. 33, pp. 101–121. [M.A. **10**–380.]

univalent K can be replaced, and O is possibly replaceable by OH. The biotite micas may therefore attain considerable Si–Al substitution values, whilst in hornblendes substitution is assisted by the presence of 'vacant positions'. Lastly, Niggli[1] has pointed out that, in magmas, the co-ordination value of Al may be determined by the amount of volatiles present. This idea has been developed by von Eckermann.[2]

With regard to the data from calciferous hornblendes; these appear to furnish another case of the general rule that, in any one mineral, the higher the temperature of formation, the higher the solid solubility of any element. The high-temperature hornblendes are therefore richest in aluminium.

As a final note, it is interesting to compare the habits of low-grade actinolitic amphiboles with those of igneous hornblendes. The latter tend to form stout stumpy prisms, whilst the former are generally of columnar, bladed, or asbestiform habit. Possibly this reflects the amount of tetrahedrally co-ordinated aluminium in each. Low values for Si–Al replacement, such as obtain in the actinolitic amphiboles, may be argued to result in weaker binding between chains of tetrahedra, favouring asbestiform developments. A high degree of replacement of silicon by aluminium, as in the magmatic hornblendes, then would favour strong links between chains and a stumpy prismatic habit. Alternatively, it may be suggested that high values for Al substitution of Si weaken the oxygen bonds binding tetrahedra into chains, therefore hinders extension of the latter during crystallization, and thus favours a stumpy form.

Acknowledgements.—The writer wishes to thank Dr. J. E. Richey for acting as communicator, Professor S. J. Shand and Dr. H. Neumann for reading the manuscript.

[1] P. Niggli, Das Magma und seine Produkte. Leipzig, 1937. [M.A. 7–2.]
[2] H. von Eckermann, Geol. För. Förh. Stockholm, 1944, vol. 66, p. 283.

An improved polarizing microscope. IV.[1] *The Fedorov stage* (*three-axis*).

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INTRODUCTION

In the microscope designed by G. B. Amici (1844), which seems to be the very earliest polarizing microscope, the stage already possessed not only graduated concentric rotation, but also a horizontal tilting axis. It was, in fact, a built-in two-axis universal stage. Glass hemispheres were introduced at a much later date by W. G. Adams (1875) for use in a specially designed conoscope, but the Adams stage seems to have been little used (see, however, H. Schumann, 1949).

The two-axis stage as now known was designed by E. S. Fedorov (1893) and was soon followed by other forms. It is a curious fact that the four-axis stage was used almost from the beginning, though it was for some time known as the three-axis stage. For example, the Swiss stage figured as a three-axis type by Duparc and Pearce (1907, vol. 1, p. 283) has four axes, and Nikitin, even in 1936 (p. 9), describes a four-axis diagram as the three-axis stage. There seems never to have been a separate early development of the three-axis stage in the strict sense, as now to be described, though a great part of the procedure for the four-axis stage really relates to three axes, the fourth axis being locked at the 90-degree position.

The explanation of this rather unexpected course of evolution can probably be found in Fedorov's original announcement of the three-axis design. There are two possible arrangements of the two inner axes, one having the tilting axis outside the concentric movement, as now, and the other with the tilting axis *inside*. When Fedorov first realized the importance of adding a third axis it was the second, unfamiliar and relatively useless, form that he illustrated (1896, p. 241). The inconvenience

[1] Parts I–III, Min. Mag., 1946, vol. 27, p. 175; 1947, vol. 28, pp. 96, 230.
[2] Published by permission of the Director.

of this design must have been obvious at once, especially since an inner concentric movement was already in use on the two-circle stage. Accordingly, an inner concentric movement seems to have been added, the result being a four-axis stage of the type used ever since. Development of the three-axis stage was, in effect, bypassed by way of the useless alternative form. Berek (1924, p. 21) says that the rapid development of the four-axis stage took place in the workshop of R. Fuess by the co-operation of Fedorov, C. Leiss, and C. Klein in the years 1895 98. Berek numbered the axes from within outwards A_1 A_4, A_5 being the axis of the microscope stage. This nomenclature will be used in the present paper, A_3 being of course absent in the three-axis stage.

In recent years the addition of a fifth axis by R. C. Emmons has provided an elegant means of eliminating computations, but the additional movement brought with it some loss in stability, and side by side with this development there has been a reverse trend in favour of the increased rigidity and simplicity obtainable with fewer axes. The two-axis stage, though widely useful, is not completely adequate, since it permits only the alinement of any chosen direction with the axis of the microscope but not the maintenance of a chosen plane. With the three-axis stage, however, it is possible to bring the normal to any desired plane into coincidence with the horizontal axis of the universal stage; by this means the crystal can be rotated so that all directions in the plane pass successively into line with the microscope axis. This is the arrangement necessary for the identification of an optical symmetry plane, an adjustment which forms the basis of ordinary universal stage procedure. The fourth axis (i.e. the outer concentric movement, A_3 of Berek) gives little further advantage, for it represents only a step in the direction more fully realized with five axes; it enables a setting to be made mechanically for which co-ordinates would otherwise have to be calculated or measured on the stereogram. It follows that if the stereographic projection is accepted and used as an integral part of the procedure, a three-axis stage will be adequate.

The importance of the three-axis stage has been very clearly defined by C. M. Gilbert and F. J. Turner (1949); they also specially stress the value of the stereographic projection not only for computation but to provide 'a clear picture of the optic and crystallographic orientation of the mineral'. So far as the writers are aware, the only three-axis stage made, up to the present, is that by the firm of Silge and Kuhne of San Francisco to a design which in all other respects closely follows the existing four-axis pattern.

It may be asked what advantage can be gained by the omission of the relatively simple outer concentric axis. The disadvantages are small, for it is rarely used even in standard four-axis procedure. In the model now to be described, by fixing the tilting axis A_2 at right angles to A_4 it has been possible to eliminate collisions between the Wright arcs and the objective. Consequently the arcs have been fixed upright, without hinges, and the lock to the spindle A_2, universally recognized as inefficient, has been replaced by clamps that slide on the Wright arcs and give complete stability when closed. Another important practical advantage is that the width of the inclinable ring has been reduced, permitting a smaller outside diameter. This not only makes the stage available for smaller microscopes, it results in a lower and more convenient distance between the horizontal axis and the microscope stage, and a shorter horizontal axis. The base of the present Fedorov stage no longer has projecting parts which cover the graduations of a standard 12 cm. microscope stage.

An improved fedorov stage (three-axis).

The stage is illustrated in fig. 1, and the new details of construction will be understood from the drawing (fig. 2). Reference has already been made to the main features that have been introduced as a consequence of the limitation to three-axis design. In addition to these developments the authors have made several independent changes in order to give greater facility in handling the stage.

1. *Horizontal axis.* –The divided circle on the A_4 axis has been separated from the knurled operating head and placed at the left-hand end of the axis. The existence of a certain discomfort in the close adjustment of this axis has been evidenced by the very large size given to the knurled head in recent models which have no slow movement. A fine adjustment has therefore been provided, as in the early model by the Société Genevoise (Duparc and Pearce, p. 283).

2. *Central plate.*—The knurled heads that usually serve to fix the metal plate bearing the upper hemisphere have been transferred to the under side of the stage, and the rather unstable small springs in these heads have been replaced by a construction in which the upper hemisphere is rigidly supported by a detachable bridge, while the whole central surface of the stage rises upon springs so that the microsection is held in position against the upper hemisphere. The sprung central plate has the great advantage that a microsection can be readily moved about by gently pressing on the ends of the glass slip so as to relieve the

pressure between the upper hemisphere and the cover-glass, care being taken not to depress the slide so far as to draw air into the interspace.

3. *Adjustment for thickness.*—Compensation for the thickness of the mounting-slip underneath the microsection, hitherto made by a shallow threaded vertical movement of the central plate, is now taken up automatically by the springs. Adjustment of the centre of the hemisphere to coincidence with the axes of rotation is made independently by rotating the threaded mount of the upper hemisphere by means of a special castellated ring on the mount which can be adjusted by the fingers from above without disturbing the normal position of the stage. The same movement also permits the interchange of hemispheres of different refractive index.

4. *Graduated net.*—Both for the selection of a suitable crystal under the microscope and for determining the thickness of a grain after optical measurement on the Fedorov stage, it is important to be able to re-locate the same grain on either instrument. For this purpose a network of $\frac{1}{2}$-cm. squares is engraved on the central plate of the Fedorov stage, and a similar net is engraved on a ring-plate which can be inserted in the stage of the microscope. The edges of the mounting-slip must be set parallel with the lines of the net. When the required grain is at the centre of the field, the co-ordinate position is read from the top and side edges of the slip (the top being identified by the writing on the label, or other distinguishing mark). To regain the same position the appropriate edges are again set to coincide with the recorded values on the grid. The numeration has been chosen so as to eliminate any possible confusion between the x and y co-ordinates or between the left- and right-hand ends of the slide. Sometimes the reading is conveniently taken at the left end, sometimes at the right, but the numbers themselves make it clear which end is being used. 0–5 belong to the right end, 9–13 to the left, and 14–19 to the top edge. If the 28×48 mm. slip is to be transferred to the Fedorov stage, the corners must not lie outside a circle of 7 cm. diameter.

5. *Area available on the microsection.* Existing four-axis stages apparently offer a fairly wide movement for the microsection, but they are in fact severely limited by the subsequent collision of the ends of the mounting-slip with projections such as the hinge-blocks of the axis A_2. For a 28×48 mm. slip the actual area of the microsection that is accessible without such collision in the case of a standard four-axis stage is defined by the outer curved lozenge shape in fig. 3 (p. 159). In the

present model the central space is free as far as the inner side of the outer tilting circle, and there are no isolated projections to cause a collision

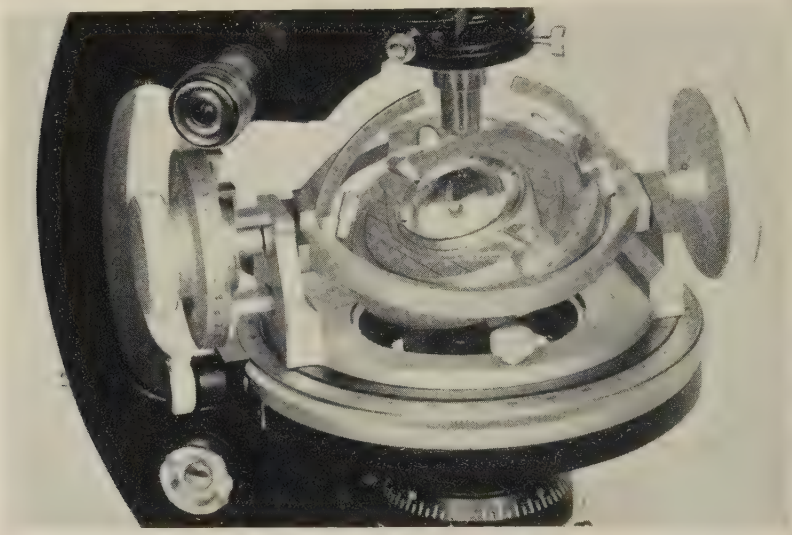

Fig. 1. Improved three-axis Fedorov stage, in place on a 12 cm. microscope stage.

Note. Clamp locking on the fixed Wright arcs; graduated net on the sprung central plate; adjustable upper hemisphere; slow-motion head to horizontal axis.

within this space. Consequently, in spite of the relatively small outer diameter, the radius of the free central space has only been diminished by $\frac{3}{4}$ mm. The actual area now available for the same mounting-slip is shown by the inner lozenge in fig. 3. A crystal that lies outside the available area can if need arises be reached in either case by cutting away the distant ends or corners of the mounting-slip. It may be noted that some firms are using slips of the size 27×46 mm. instead of the usual 28×48.

6. *To insert an object-slip.*—A_4 is locked at zero and the central part of the stage is fixed in an inclined position by means of the lock on one of the Wright arcs. A small amount of immersion liquid is placed on the middle of the upper and lower surfaces of the object-slip. The central plate of the stage is depressed by the left hand while the slip is inserted under the upper hemisphere.

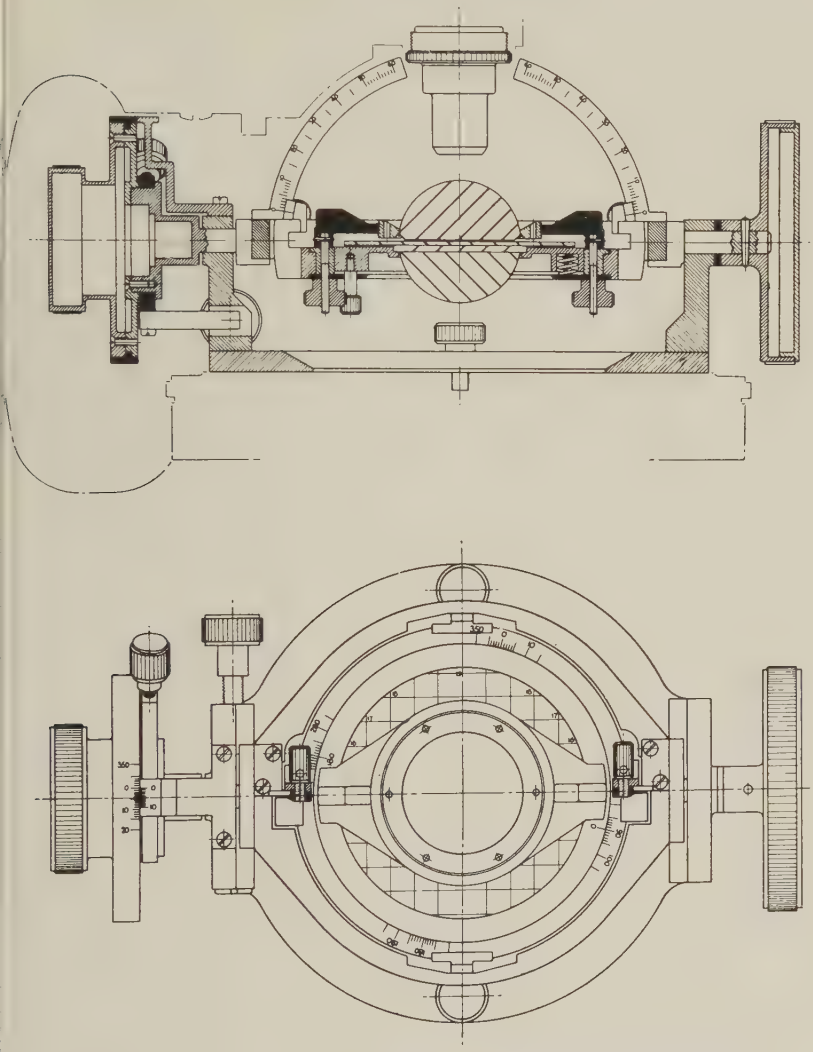

FIG. 2. Improved three-axis Fedorov stage (plan and section).

PRELIMINARY ADJUSTMENT AND CHECKING.

The above instrumental changes, and the introduction of new methods for hemisphere adjustment and in place of autocollimation, entail substantial changes in the text-book routine for adjustment. A brief outline of these will now be given. As will be seen, some parts of the old

procedure are still available. On the other hand, some new methods can be applied to the older types of stage.

In discussing the title of his work 'Mineralbestimmung' Berek (1924, preface, p. ix) pointed out that the universal stage should be regarded as an accurate means of determining minerals in general, as well as the less strongly birefringent felspars. For this reason it will be necessary to consider the adjustment of microscope and stage with greater care than would otherwise be needed.

Apart from the initial difficulty of exactly identifying and adjusting an optical symmetry plane, cleavage, &c., and the effect of difference in refractive index between crystal and hemisphere, the chief sources of error are: (1) in the microscope used, incomplete alinement of the optical axis and that of the stage; (2) imperfect centring of the upper hemisphere to the axes of rotation; and (3) small errors due to graphical methods. The errors inherent in the mechanical construction of the Fedorov stage itself are usually well within the limits required, but 'zero readings' may in some cases have to be ascertained for subtraction from the observed angles.

A. *The microscope stage and axis.*

It will be assumed that the polarizing system and cross-lines of the microscope are already in correct adjustment. Both for general convenience and for the accurate measurement of extinction with the biquartz and of path difference with the quartz wedge, a Dick-Wright ocular is to be preferred. On the smaller microscopes the objective should be attached directly under the hand-centring screws, in the place of the vertical illuminator (fig. 1).

1. *Axial alinement.*—Two methods have been proposed for verifying the alinement of a rotation axis, in this case that of the microscope stage, with the optical axis of the microscope. Of these, autocollimation has nearly always been employed, but the alternative, which may be termed the 'Nachet method', will here be preferred. For autocollimation some more or less elaborate arrangement is fitted, in which the image of a mark in the microscope is reflected by a glass surface parallel with the microscope stage. The coincidence of the mark with its reflected image indicates that the stage is normal to the axis. Sometimes only the image of a mark fixed on the mechanical axis is reflected on to the cross-lines in the eyepiece, the mark itself not being visible. Illumination is often difficult, and autocollimation may be said to be generally rather difficult and troublesome in practice.

2. *The Nachet method.*—This very interesting method, hitherto almost completely neglected, is described by Wülfing (Rosenbusch, 1922, p. 431) and is particularly suitable for the present purpose. It is based upon a construction used in the early Nachet microscope, and we have accordingly referred to it by this name. A slide of strewn dust or a fine ground glass is placed on the microscope stage. The objective is removed from the tube and is supported in a short tube of metal or paper at its usual working distance above the slide. Thus an image of the object is still formed in the eyepiece, but when the stage is rotated the objective rotates with it instead of being fixed to the tube. When the stage is turned, the image in the eyepiece rotates about a point which marks the intersection of the mechanical axis of rotation of the stage with the focal plane of the eyepiece. It is easy to verify that the position of this point is in no way affected by the nature of the objective or its position (provided that it transmits light in the required direction) or by the flatness or quality of the object if of suitably fine grain. The apparent centre of rotation in the eyepiece is easily identified, and the degree of coincidence with the cross-lines can be checked, preferably with the eyepiece net micrometer (1 mm. squares). If the distance from the cross-lines to the stage is, say, 200 mm., a lack of coincidence of 1 mm. will represent an error of 17 minutes. In the ordinary use of the Fedorov stage this is probably a suitable upper limit, but closer agreement may be advantageous. If desired the correction may be measured and applied to the readings.

The objective may now be replaced on the microscope and centred in the usual way. When this has been done, the effective optical axis of the microscope is the line joining the centre of the stage to the cross-lines. No appreciable defect is caused because the objective is not perfectly coaxial within the present limits.

B. *Adjustment of the Fedorov stage and determination of zero readings.*

After removal of the ring-plate from the centre of the microscope stage, the Fedorov stage can be attached by two fixing-screws that engage with holes in the microscope stage. The knurled head of the main horizontal axis should be on the right-hand side and the microscope stage at zero.

1. *Centring* (usual method).—With the Fedorov stage at zero markings the microscope is focused on a slide, in theory without the upper hemisphere; the microscope stage is rotated and the centring of the objective is corrected if necessary, so that the centre of rotation of the

image coincides with the cross-lines. The microscope stage is then locked and the innermost circle A_1 of the Fedorov stage is rotated. If the centre now obtained does not coincide with the cross-lines the fixing-screws must be somewhat loosened while the Fedorov stage is moved till correct centring is obtained. In practice the hemisphere may be in place.

2. *Axial adjustment.* (Nachet method). —Lock the Fedorov stage at the zero markings and place the objective in the short tube on a ground-glass slip as described above, or in a special tube fitting above the hemisphere. On rotating the innermost circle A_1, the point of intersection of its axis with the focal plane of the eyepiece can be identified. It should coincide with that of the microscope stage axis, which can be at once re-located by rotating the microscope stage. As in the case of the microscope stage axis, a difference of 1 mm. represents about $\frac{1}{4}$ degree. If the error seems important for the class of work that is being undertaken, bring the two centres into coincidence by slightly inclining the section about the axes A_2 and A_4. Lock these axes and read the values, which are the zero readings for the respective divided circles, and are to be subtracted from the observed angles. For this purpose coincidence should be obtained with the microscope stage axis, not the cross-lines, for which the error has already been estimated (para. A 2 above).

N.B. The Nachet method is sensitive to centring as well as to the inclination of the axis, and operation (1) above must always be completed before the Nachet method is used.

3. *Zero reading for the microscope stage* (Berek, 1924, p. 36).—Place the upper hemisphere in position and focus the microscope on specks of dust, &c., on the upper surface of the hemisphere. When the horizontal axis A_4 is turned, the image of the dust should traverse the field parallel with the N.–S. cross-line. To bring a dust particle nearer to the cross-line, incline the hemisphere a little about the A_2 axis. Dark ground or top lighting may be helpful. If the movement is not parallel with the cross-line, rotate the microscope stage till this adjustment is obtained. The angle then read on the stage vernier is to be subtracted as a zero reading from the readings for any rotation that may be measured on the microscope stage.

4. *Verification of the intersection of the tilting axes A_2 and A_4* (usual method).—Focus the microscope through the upper hemisphere on a microsection *with normal thickness of cover* (see (5) below). Rotate about the horizontal axis A_4 and note whether the points in the image appear to move across the field. If they do so, adjust the height of the hemisphere by turning the threaded mount which has been provided with

castellations for this purpose. When the movement has been eliminated, the edges of the field will go out of focus as A_4 is inclined, but a band parallel with the A_4 axis will remain stationary and in focus. This should cross the centre of the microscope field. Similarly, without further adjustment, when A_4 is at zero, a band at right angles to the first can be identified by inclining the section about A_2. If the image does not remain nearly steady when the second axis A_2 is turned, the second axis is either above or below the first. This condition is rarely

Fig. 3.

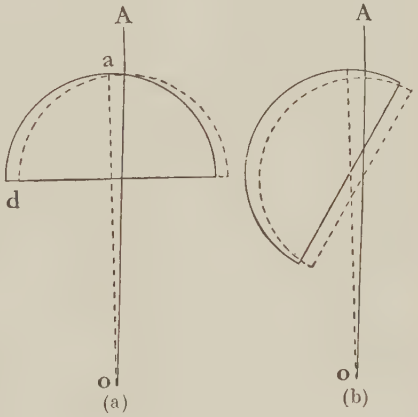

Fig. 4.

Fig. 3. Centre of Fedorov stage.
Fig. 4. Deviation of axial line in a displaced hemisphere.

found. If present, it can only be remedied by returning the stage to the factory. A new and more sensitive method is given below (5).

5. *Centration of the upper hemisphere.*—Little or nothing has been said in most text-books about the refractive effect of the glass–air surface of the hemisphere. *Principle involved*: Let A (fig. 4a) be the optical axis of the tube and objective and Fedorov stage when in proper adjustment. The centre of the hemisphere when correctly adjusted should lie on this line. Suppose the hemisphere is displaced laterally by a distance d. The direction A now undergoes refraction on entering the hemisphere and converges upon o, the principal focus of the upper surface. The distance ao may be taken as approximately three times the radius of the hemisphere. For a hemisphere of radius 12 mm. a lateral displacement d equal to 1 mm. will therefore cause a deviation of $\frac{1}{36}$ radian = 1·6 degrees.

If a maximum tolerance of $\frac{1}{4}$ degree is accepted, the hemisphere must be centred within 0·17 mm.

The effect of displacing the hemisphere in this way may be demonstrated as follows. With a little oil attach a microsection to the central glass plate and centre the microscope and Fedorov stage as usual. With the stage locked at zero place one of the loose (under) hemispheres upon the microsection, with enough oil to enable it to slide about freely without disturbing the object. When the previous centration is again checked it will be found that the centres of rotation have not been displaced by the presence of the hemisphere, even if it is badly off centre. This is an example of the Nachet principle already described. As the hemisphere is displaced, however, the image moves across the field. Only when the hemisphere is truly centred will the point imaged on the cross-lines be the same as that seen without the hemisphere.

Test for central mounting.—It follows that displacement of the hemisphere could pass completely unnoticed during the ordinary tests by rotation. The mounting of the hemisphere does not usually cause any noteworthy error. It may be checked by centring an isolated particle on the cross-lines as above and then placing the upper hemisphere in position. The image of the particle should still be found on the cross-lines, within the tolerance allowed. For an error of $\frac{1}{4}$ degree this will be an apparent distance $\frac{2}{3}d$ on the object, 0·11 mm. The error is best measured by inserting a micrometer net in the eyepiece. With a $\times 5$ objective ($\times 7{\cdot}5$ with hemisphere) one may say that the image must not be displaced by more than 0·7 mm. in the focal plane of the eyepiece.

The objective stop.—In the conoscopic system (if the Bertrand lens is used with the cross-lines for the present purpose it must be in accurate adjustment with the optical axis already established) the back of the 0·15 N.A. objective includes a conoscopic angle of about 17 degrees *inside* the hemisphere. A circular stop one-tenth of the objective diameter will include $\pm 0{\cdot}8°$. If a small light-source is imaged without the stop through the loose hemisphere, the change of direction due to displacement of the hemisphere can be demonstrated by the movement of the spot of light at the back of the objective. Seen in this way the effect does not seem very large, but such displacements are comparable with the accuracy of adjustment attainable for a narrow zero isogyre or for a favourable extinction setting in the orthoscopic system. For accurate results, the use of the small stop seems inevitable; it may conveniently be directly centred to the back of the objective, and is preferably an iris.

Vertical adjustment of the hemisphere.—No universal stage has so far

been provided with means for altering the distance between the microsection and the hemisphere: the two move together. The hemisphere is really a segment with an allowance (0·007 inch) for the thickness of cover-glass and balsam above the section. If the thickness of cover differs from this value, the section when adjusted in the axis of rotation will not contain the centre of the hemisphere, which will be too high or too low. Since, however, the tolerance as above (see fig. 4b) will be about 0·17 mm., serious error can only arise when the microsection is too low, i.e. when the cover is too thick. When the adjustment of height is made in the usual way (para. 4 above), the position at which the object appears to be stationary is really a compromise between the effects of two displacements, of the hemisphere centre and of the microsection. The usual method is only valid if the cover is of standard thickness.

In the present design the hemisphere is independently supported by the bridge, and if it has been adjusted to coincide with the rotation axes (by using a correctly covered section or as below), the microsections should be interchangeable without readjusting the hemisphere for height. In this case any different thickness of cover will be evidenced at once by the displacement of the image on rotating about A_2 or A_4. If excessive it is best eliminated by re-covering the microsection with a suitable cover-glass. Although small movements of the image may cause inconvenience, a low position of the microsection is not in itself a cause of error, since angles alone are in question. It would seem that for the most accurate measurements the hemisphere should be kept fixed in the bridge at the proper height, at which its centre coincides with the intersection of the stage axes.

A very accurate direct test of the height of the hemisphere can be made as follows. An objective of shallow focus, say 4 mm., is focused on the surface of the hemisphere. Readings for the position of the surface are made on the micrometer fine-focusing screw. On inclining the hemisphere about the axis A_4 or A_2, the reading for the zero position should be midway between those for the greatest inclination on either side. If not, the microscope micrometer can be set to the desired reading and the hemisphere (at zero) raised or lowered in the screw-mount to the correct level. The test is very sensitive, and a difference of about 0·1 mm. is permissible between the inclined readings. This difference is a test of the centring of the hemisphere horizontally on the axes A_2 and A_4. When the height is correct the height-curves are centro-symmetrical and nearly linear.

6. *Other verifications.*—Several other tests are well known or will

suggest themselves; they need not be discussed in detail since the results rarely reveal any error. Thus, after (3) the angle of 90 degrees between the cross-lines can be checked by rotating the microscope stage through 90 degrees and moving the dust particle parallel with the other cross-line. Again, in the same way, by inclining first about A_4 and then about A_2, it can be verified that these two axes are at right angles to one another.

The tests in the last three sections (4 to 6) will not need to be repeated for the same instrument unless the hemisphere has been disturbed, but it will always be advisable to carry out the first three checks as a preliminary to making a series of measurements, in case the Fedorov stage has been displaced. The authors believe that, owing to the introduction of the Nachet method, it has now become possible to make a complete zero check with great facility and accuracy. During use the centration of the image should be checked occasionally by rotating the microscope stage, to make sure that the centring of the objective has not been disturbed. A section with correct thickness of cover may be kept for adjusting the height of the hemisphere.

References

Adams (W. G.), Phil. Mag., 1875, ser. 4, vol. 50, p. 13.

Amici (G. B.), Ann. Chim. Phys., 1844, ser. 3, vol. 12, p. 114.

Berek (M.), Mikrosk. Mineralbestimmung . . . Universaldrehtischmethoden. Berlin, 1924. [M.A. **2**–365.]

Duparc (L.) and Pearce (F.), Traité de technique . . . Pt. I. Les méthodes optiques. Leipzig, 1907.

Emmons (R. C.), The universal stage. Mem. Geol. Soc. Amer., 1943, no. 8. [M.A. **9**–18.]

Fedorov (E. S.), Zeits. Kryst. Min., 1893–94, vols. 21–22; 1896, vol. 26, p. 241.

Gilbert (C. M.) and Turner (F. J.), Amer. Journ. Sci., 1949, vol. 247, pp. 1–26. [M.A. **10**–467.]

Nikitin (W.), Die Fedorov-Methode. Berlin, 1936. [M.A. **6**–433.]

—— La Méthode universelle de Fedoroff. Trans. L. Duparc, vol. 1, Geneva, 1914.

Schumann (H.), Zeits. angew. Physik, 1949, vol. 1, p. 343.

Wülfing (E. A.), in H. Rosenbusch, Mikrosk. Physiographie, vol. I, pt. 1. Untersuchungsmethoden. 5th edit., revised by E. A. Wülfing, Stuttgart, 1921–24. [M.A. **1**–358.]

Postscript.—In figs. 1 and 2 the hemisphere mount has been since replaced by a castellated ring operated by the fingers, which does not cause the hemisphere to rotate during adjustment.

Dichroscopes for microscope stage and ocular.

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[Read November 10, 1949.]

THE optical accessories here described are two dichroscopes to facilitate microscopical comparisons by eye between the hues and intensities of axial absorption colours shown by thin slices, crushed fragments, or detrital grains of transparent coloured doubly-refracting crystals. Their chief applications lie in microscopic mineralogy and petrology, but they can be of service, also, in chemistry and allied subjects.

The aims of the accessories are two in number. They provide: (i) simple microscopic means for viewing simultaneously any pair of distinct hues, intensities of hue, or combinations of these variables, which result from differential absorption of white light; and (ii) a convenient method for detecting small differences between any pair of hues, intensities, or both, in terms of immediate ocular comparison between two sets of small symmetrically-shaped coloured images which alternate, and meet in straight boundaries. Neither advantage (i) nor (ii) above is afforded by the petrographic microscope when employing only the polarizer in the optical system (Tschermak's method, 1869) (1); while if the alternative is adopted of using only the analyser in the optical system the interpretation of such pleochroic tints as are seen can be complicated by effects due to a variable proportion of polarized light reflected at the surface of the microscope mirror (2).

Both the grating and chequer types of these accessories, composed of polaroid, are adapted for use either on the stage or in the ocular of a petrographic or other microscope.

The *grating type* (fig. 1 *a*) yields a field divided into a set of narrow parallel bands of equal width, alternate bands of which show one of the two absorption tints or intensities of tint concerned. The resulting subdivision and interdigitation of the two equal areas of distinct hue or intensity enables a considerably more accurate estimate of such differences to be made by eye than is possible when the areas are discrete, and the two halves of the field meet in a single straight boundary, as is the

case with the image seen in the hand-dichroscope (dichroskopische Loupe of W. Haidinger) (3).

In the *chequer type* (fig. 1 *b*), on the other hand, the centre of the field is occupied by a small square subdivided into four smaller squares of which diagonally-opposed pairs show the same absorption hue or intensity, while adjacent pairs show the two different absorption hues or different intensities involved.

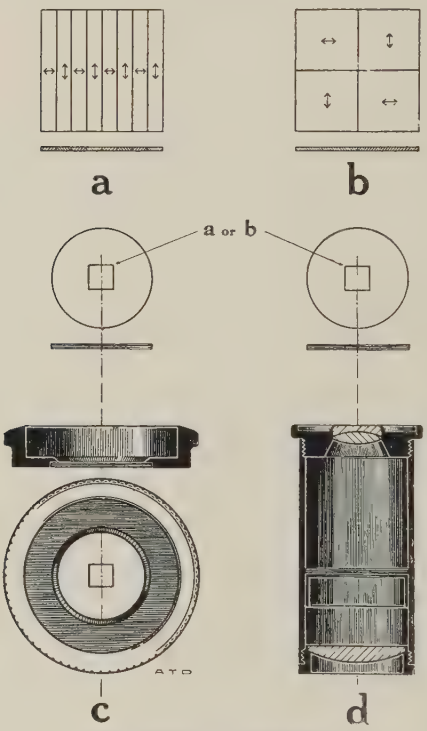

Fig. 1. Microscope dichroscope. *a*, grating type. *b*, chequer type. *c*, for stage. *d*, for ocular.

The *stage adaptation* of either the grating or chequer type (fig. 1 *c*) has the advantage that it can be introduced over a mounted pleochroic crystal without change in any adjustment of the microscope other than focus. Experience shows that these types function more efficiently on the microscope stage than in the accessory slot of the body tube.

The *eyepiece adaptation* of either type (fig. 1 *d*) has the advantage that: (i) it can be made to cover less than 4 % of the field, and thus does not interfere markedly with optical observations other than those of differential absorption; while (ii) it can be turned through any desired angle by rotating the eyepiece in the body tube, thereby enabling the accessory to be set in such a position relative to the crystal concerned that extreme differences of hue or intensity are visible for direct inter-comparison. This latter is the method appropriate to those microscopes with non-rotating stages, but when a rotating stage is fitted the same result can be obtained with equal ease by centring the crystal and then revolving it through the necessary angle on this stage, while leaving the eyepiece stationary.

The chief disadvantage of this adaptation is that it cannot be removed from the microscope ocular without unscrewing the eye-lens of the latter.

Generally the grating type of these accessories is better suited for studies of pleochroism in small elongated crystals than the chequer type, which serves for corresponding determinations on small but more nearly equidimensional crystals.

Functionally, both varieties of dichroscope behave in the same manner as the hand-instrument described by W. Haidinger in 1845 (3), but they differ from it in being (i) designed for microscopic rather than macroscopic use and in being (ii) constructed of small plates of polaroid in place of a prism of Iceland-spar. That the improved polaroid now available is a suitable substitute for Iceland-spar in this respect is evidenced by the investigations of Dr. A. F. Hallimond (4) into its efficiency as a polarizing medium and by those of Dr. J. McClelland (4) on its 'remarkably uniform' absorption over nearly the whole range of the visible spectrum, apart from a 'slight increase in absorption of the blue-green'. The latter is not a serious factor in practice.

The operation of the ocular adaptation of these accessories is comparable with that of the dichroscope ocular devised by C. Leiss in 1897 (5), but differs from it in being due to a group of small square plates of polaroid, as opposed to a prism of Iceland-spar. In employing polaroid plates, this latest dichroscope ocular resembles one suggested ten years ago by N. W. Thibault (6).

The polarizing medium.—The modern 'polaroid'[1] used as the light-polarizing medium in these two types of stage and ocular dichroscope is a development of an invention by the physicist E. H. Land (7). It is understood to be a thin sheet of a molecularly orientated linear polyvinyl oxy-compound (e.g. polyvinyl alcohol), or its equivalent, incorporating an iodine-bearing dichroic stain. Usually the linear molecular orientation of the plastic base would appear to be effected by appropriate stretching of the sheet, while the associated dichroic stain is protected from changes due to moisture, heat, or ultra-violet radiation by one of several special treatments of the surface of the sheet during production.

Since this latest kind of polaroid, patented in 1945 (8), differs from that patented during 1934, 1935, and subsequently (7) in being (i) more stable, both physically and chemically, and in (ii) transmitting light of a more nearly neutral tint, it is to be preferred in the dichroscopes described, but the efficiency of the earlier kind in these connexions is closely similar.

This earlier variety has been described as a uniformly distributed and flow-orientated suspension of elongate sub-microscopic crystals of the

[1] Manufactured by the International Polaroid Corporation, U.S.A.

strongly dichroic quinine sulphatoperiodide, 'herapathite'[1] (9), some allied alkaloid compound, or the inorganic compound purpureocobalt-chloride-sulphate-periodide (10), occupying the central layer of a thin cellulose nitrate or cellulose acetate sheet.

Optically, such a sheet behaves as a single thin crystal. Further, since the minute constituent crystals cannot be seen, even when magnified 1100 diameters, the sheet shows no structure under the microscope, though it is estimated there are about 10^{12} of them per square inch of sheet, and the uniformity of polarization throughout the sheet suggests they are distributed and alined with corresponding uniformity (11).

It has been shown that the degree of polarization of white light achieved by such a piece of polaroid varies between 95 and 98 % for the range 5000 to 6500 Å., i.e. for that part of the visible spectrum to which the human eye is most sensitive (12).

The faint neutral tint of the light transmitted by such a sheet has been described as 'similar to that of lightly smoked glass' (11). The amount of light so transmitted constitutes about 33 % of the incident light, as compared with nearly 50 % of the incident light passed by a nicol prism (4).

Practical importance attaches to the fact that both the earlier and later varieties of polaroid are stable up to temperatures in the neighbourhood of 120° C., for on this account they can be mounted permanently in 'cooked' Canada balsam without detriment to their polarizing properties.

Lastly, neither variety shows appreciable deterioration with age, as is evidenced particularly by the results of thermal and optical tests carried out recently by the author on pieces of the earlier types of polaroid which have been in his laboratory for the past nine years.

Construction.—To fulfil the optical requirements of the dichroscopes under discussion it is necessary to derive from polaroid: (i) rectangular plates $2 \times 0{\cdot}25 \times 0{\cdot}07$ mm.; or (ii) square plates $1 \times 1 \times 0{\cdot}07$ mm., which in either case can be mounted so that they fit together very closely, edge to edge, with the polarization axes in adjoining pairs of plates orientated at 90° to each other. Means were sought for cutting sets of parallel-sided strips 0·25 and 1 mm. wide respectively, in each set of which half the number had their polarization axes parallel to the *lengths* of the strips while the other half had their polarization axes parallel to the *widths* of the strips.

At first, experimental strips were cut and subdivided with sharp

[1] $4Qu.3H_2SO_4.2HI.I_4.6H_2O$.

surgical scissors, but while the resulting plates established the general efficacy of the dichroscopes so produced, when arranged and mounted appropriately, their edges were so burred, serrated, and chipped that an inadequate fit was obtained between them. Similar though slightly improved results were obtained with a large photographic print-trimmer and a printer's guillotine. Ultimately suitable strips, some 80 mm. in length, were cut by hand with a stiff mounted safety razor blade, using plate-glass as a base and a steel straight-edge as a guide.

From the resulting strips a careful selection was made by means of a petrographic microscope, employing an eyepiece micrometer for checking widths and parallelism between pairs of long edges of the strips, and the polarizer for checking the directions of their polarization axes.

In assembling the grating type of this dichroscope (fig. 1 *a*) eight strips 0·25 mm. in width, about 40 mm. in length, and 0·07 mm. in thickness were chosen, four of them with their polarization axes parallel to their lengths and four with their polarization axes perpendicular to their lengths. Strips were then placed alternately and laid approximately parallel to each other on a plate-glass sheet, slid with the finger tips into the closest possible contact, edge to edge, and then held thus, and to the glass, by small cakes of plasticine pressed down across their ends.

Next, a length of about 20 mm. in the centre of the resulting group of parallel strips was cemented into a continuous ribbon by a thin coat of 'D.P.X. balsam'[1] which was applied across and between the strips with a small soft brush. As soon as this coat had hardened the plasticine cakes were removed, the ribbon peeled from the glass, a length of 2 mm. cut from the centre of its cemented portion with a safety razor blade, and the resulting square mounted centrally between two circular cover-slips [22 mm. ($\frac{5}{8}$ inch) diameter] with 'cooked' Canada balsam. Thus by means of this 'D.P.X. balsam' both malalinement of the small plates of the grating and the development of bubbles between them was prevented, without introducing any optical disadvantage thereby.

Prepared in this way the grating can be cemented into the base of the brass ring shown in fig. 1 *c*, for use as a microscope-stage dichroscope, or placed on the diaphragm of a microscope eyepiece (fig. 1 *d*), when it constitutes an ocular dichroscope.

To assemble the chequer type of this dichroscope (fig. 1 *b*), four squares, each $1 \times 1 \times 0{\cdot}07$ mm., were cut with a safety razor blade from a strip of polaroid $1 \times 40 \times 0{\cdot}07$ mm., the polarization axis of which was parallel to its length. These four small square plates were then laid edge to edge

[1] 'Distrene 80', 10 gm.: butyl phthalate, 5 c.c.: xylol, 35 c.c.

in a thin tacky layer of 'D.P.X. balsam' on a plate-glass sheet to form a large square with the small squares so orientated relative to each other that the respective polarization axes of the two diagonally opposite pairs were parallel but the polarization axes of adjacent pairs were perpendicular.

After pressing the plates into intimate contact with each other by means of square-ended tweezers a thin layer of 'D.P.X. balsam' was brushed over the plates to fix their relative positions and prevent bubbles developing between their edges during subsequent mounting. When this balsam had hardened the resulting chequered unit, consisting of four polaroid plates embedded in it, was stripped from the glass, and then mounted centrally between two circular cover-slips [22 mm. ($\frac{5}{8}$ inch) diameter] in hot Canada balsam.

As with the grating type of this accessory, such a mount of the chequer type can be cemented into the base of the brass ring shown in fig. 1 *c*, for use as a microscope-stage dichroscope, or slid on to the diaphragm of a microscope eyepiece (fig. 1 *d*) to give an ocular dichroscope.

The form of the small metal holder for the stage adaptations of these accessories is illustrated in fig. 1 *c*. It consists of a rhodium-plated brass ring, 32 mm. in diameter, and 6·5 mm. in maximum depth, with a central circular aperture 13 mm. in diameter. A knurled outer rim 2 mm. in width facilitates the manipulation of the ring on the microscope stage. A recess 1·5 mm. in depth is cut in the base of the annulus, about the viewing aperture, to receive either a mounted grating or chequer dichroscope unit which is cemented in position by a convenient plastic varnish so that its lower surface is flush with that of the ring. The surface of the recess in the upper side of the ring is coated with matt black paint, to avoid unwanted reflections of light.

Operation.—Polarizer and analyser are withdrawn from the optical system of a petrographic microscope and a crystal grain is focused and centred under an objective of low or medium power, using unpolarized white light of the highest convenient intensity for illumination.

(*a*) *Stage adaptation.*—The base of the brass ring which contains the polaroid dichroscope unit (fig. 1 *c*) is held in contact with the cover-slip between finger and thumb; the dichroscope plates are centred over the crystal grain and the latter re-focused through this group of plates. Then, to observe and compare the absorption effects involved: either (i) the specimen is rotated beneath the dichroscope plates by revolving the stage; or (ii) the dichroscope unit is turned above the stationary crystal grain by revolving the brass ring between finger and thumb until

either a maximum difference of hue or intensity of one hue is shown by adjacent pairs of rectangular or square plates, depending on whether the grating type or chequer type of the accessory is concerned.

When using the grating type, detection of the small differences of hue or intensity shown by pairs of adjacent plates can be facilitated by oscillating the group of plates across the specimen at a frequency of about four per second in a direction parallel to the widths of the plates.

Similarly, when employing the chequer type, improved perception of these small differences of hue or intensity can be obtained by giving such a bodily rotation of the brass ring, between finger and thumb, without turning it about its centre, that the centre of the square formed by the polaroid plates revolves in a small circle within the periphery of the image of the crystal grain. For this purpose a frequency of between two and four revolutions per second will suffice.

(*b*) *Ocular adaptation.*—An eyepiece bearing either type of polaroid dichroscope unit on its diaphragm (fig. 1 *d*), is inserted in the microscope, after which the crystal grain is focused and centred at the intersection of the cross-wires, i.e. the centre of either dichroscope unit.

Then, for comparison of the absorption effects: either (i) the dichroscope is rotated by revolving the ocular in the body tube, while leaving the stage and crystal stationary; or (ii) the crystal is rotated on the stage, while keeping the ocular stationary, until the maximum difference between two hues or intensities is seen.

It will be noticed that in this adaptation of the accessory the image of either the grating or chequer group of dichroscope plates and that of the crystal grain can be brought into focus simultaneously, whereas with the stage adaptation the image of either group of dichroscope plates is slightly out of focus when that of the crystal is in sharp focus.

To aid in the detection of small differences of hue or intensity by means of this form of the accessory, the glass slide carrying the specimen may be oscillated beneath the stationary grating dichroscope, or rotated bodily beneath the stationary chequer dichroscope, at a frequency of about four per second in either case.

(*c*) *Precautions.*—In using any one of these dichroscopes to the best advantage the light employed to illuminate the specimen should be: (i) white; (ii) not appreciably polarized before meeting the specimen; and (iii) of an intensity such that, at the ocular of the microscope, it gives rise to bright colour-images subtending suitable angles at the eye. Further, the observer should know the kind and degree of any colour defect of his eyes, considered individually, and in terms of this know-

ledge should use the more appropriate eye for sufficiently short periods of time to avoid errors due to retinal fatigue.

Of white light from natural sources, diffused sunlight from a sky entirely covered with white cloud is preferable to that from a partially-clouded or unclouded sky, particularly as regards degree of polarization (13). However, if the intensity of this light is insufficient to give the necessary bright images, then an artificial source will serve if used in conjunction with appropriate colour filters (14).

Inaccuracies in these studies can result from the use of partially-polarized light reflected by the microscope mirror. A. Johannsen would appear to regard this polarization as arising during reflection of the light at the mirror, and consequently recommends dispensing with the latter and so inclining the microscope as to receive light directly reflected from the sky or clouds (15). However, in this same connexion, T. Crook states that while such a microscope mirror is unable to produce any appreciable degree of polarization of incident light, it can and does reflect naturally polarized sky-light (16).

As early as 1809 Arago showed that light from a clear sky is partially polarized. It is now known that the maximum proportion of such polarized light (usually about two-thirds) is propagated from a region in the solar vertical and about 90° from the sun, except for three small neutral points in or near to the solar vertical, the light from which is unpolarized. For a solar altitude in excess of 20° the plane of polarization of light from this region departs little from that including the sun, the observer, and the observed point. The degree of polarization and the positions of the neutral points at any given moment depend upon the wave-length of the light concerned, the altitude of the sun, and the degree of turbidity of the atmosphere (17). Hence, when making such dichroscopic determinations as have been described, unqualified acceptance of the suggestion that 'at ordinary magnifications a good north light with a broad clear sky forms an excellent source of illumination for the polarizing microscope' (18) may introduce errors, especially if these determinations are made in the early forenoon or late afternoon.

When a calcite polarizer in a petrographic microscope is revolved as rapidly as possible the least intensity-fluctuation produced in the beam of light reflected through it from the mirror, as seen in the eyepiece, indicates a minimum polarization of about 20 % (19). A comparable result can be obtained by using either the grating or chequer type of dichroscope unit here described, or a single sheet of polaroid on the rotating stage, in place of the calcite polarizer mentioned above.

As the acuity of the human eye is practically the same for both red and blue light of medium intensity, but different when these are of low intensity—the 'Purkinje phenomenon'—it follows that the illumination of the specimen under the microscope should be of sufficient intensity to avoid this source of error (20). Also the coloured field should subtend not less than 2° at the eye if a restricted chromatic response of the retina is to be avoided (21).

Since not less than 8 % of males and about 0·5 % of females have grossly abnormal colour vision, and an additional percentage of each sex possesses the defect to a distinct though more limited extent, this factor should not be neglected in ocular studies of pleochroism, especially by male observers (22). Of such people the greater number show this abnormality in both eyes, but a few—possibly 3–4 % of the colour blind—possess it in one eye (23).

On account of the colours confused and the frequency with which it occurs, congenital red-green blindness is a most important type, affecting about 5·6 % of males (22). In mild cases the ability to distinguish between red and green fails when the intensity of illumination lies below a critical value, or the individual is fatigued, or both conditions apply (23).

Finally, apart from these congenital colour defects there are acquired types due to certain pathological conditions of the eye, or to such causes as excessive smoking (24), for example.

Utility.—With a suitable kind and intensity of illumination the two types of dichroscope described provide means for direct quantitative and qualitative ocular comparison between pairs of absorption tints of pleochroic crystals under either the polarizing or non-polarizing microscope by symmetrically subdividing and alternating the parts of two coloured images of equal size, which images can be compared in contact with each other across a number of straight boundaries. In this way either of these types of dichroscope enables small differences between two absorption tints, or between two intensities of one absorption tint, to be detected which could pass unnoticed when seen in succession.

On account of the very faint absorption tint shown by modern polaroid itself, this material is slightly more efficient as a means for detecting small differences of intensity of one absorption tint than it is of differentiating between two nearly identical absorption tints of the same intensity.

Either stage adaptation of these accessories can be introduced into, or withdrawn from, the optical system of the microscope without disturbing any previous adjustment except focus. On the other hand, either

ocular adaptation can be brought into operation immediately by centring a crystal grain at the intersection of the cross-wires, whereas at other times the large area of the field not covered by the groups of polaroid plates allows of many optical determinations not involving differential absorption.

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References.

1. Tschermak (G.), 1869. Sitz.-ber. Akad. Wiss. Wien, vol. 60, p. 5.
2. Johannsen (A.), 1918. Manual of petrographic methods. New York, pp. 320, 326.
3. Haidinger (W.), 1845. Pogg. Ann., vol. 65, p. 4.
4. Hallimond (A. F.), 1944. Nature, London, vol. 154, p. 369. [M.A. **9**–116.]
5. Leiss (C.), 1897. Neues Jahrb. Min., vol. 2, p. 92.
6. Thibault (N. W.), 1940. Amer. Min., vol. 25, p. 88. [M.A. **8**–77.]
7. Land (E. H.), 1934. British Patent, no. 412,179; 1935, British Patent, no. 429,925; 1935, British Patent, no. 433,455; 1941, Canadian Patent, no. 401,436.
8. International Polaroid Corporation, 1945, British Patent, no. 573,474.
9. Herapath (W. B.), 1852. Phil. Mag., ser. 4, vol. 3, p. 161; 1853, vol. 6, p. 346; 1855, vol. 9, p. 366.
10. Land (E. H.), 1935. British Patent, no. 433,455.
11. Engineering, 1936, vol. 162, pp. 235–236.
12. Pollard (A. F. C.), 1937. Polaroid and polarized light. London, p. 6.
13. Minnaert (M.), 1940. Light and colour in the open air. London, p. 253.
14. Davis (R.) and Gibson (K. S.), 1941. U.S. Bur. Standards, Misc. Pub. no. 114.
15. Johannsen (A.), 1918. Manual of petrographic methods. New York, p. 326.
16. Crook (T.), 1911. Min. Mag., vol. 16, footnotes pp. 19, 20.
17. Busch (F.) and Jensen (C.), 1911. Tatsachen und Theorien der atmosphärischen Polarisation. Jahrb. Hamburg. Wissenschaft. Anst., vol. 28 (for 1910), Beiheft 5, pp. 1–532.
18. Rogers (A. F.) and Kerr (P. F.), 1933. Thin-section mineralogy. New York, p. 24. [M.A. **5**–433.]
19. Wood (R. W.), 1947. Physical optics. New York, p. 339.
20. Pirenne (M. H.), 1945. Proc. Cambridge Phil. Soc., vol. 42, p. 78.
21. Willmer (W. N.) and Wright (W. D.), 1945. Nature, London, vol. 156, p. 119.
22. Wright (W. D.), 1946. Researches on normal and defective colour vision. London, p. 303.
23. Collins (M.), 1937. Presidential address, Sect. J (Psychology) Rep., Brit. Assoc., p. 210.
24. Edridge-Green (F. W.), 1909. Colour-blindness and colour-perception. London, p. 227.